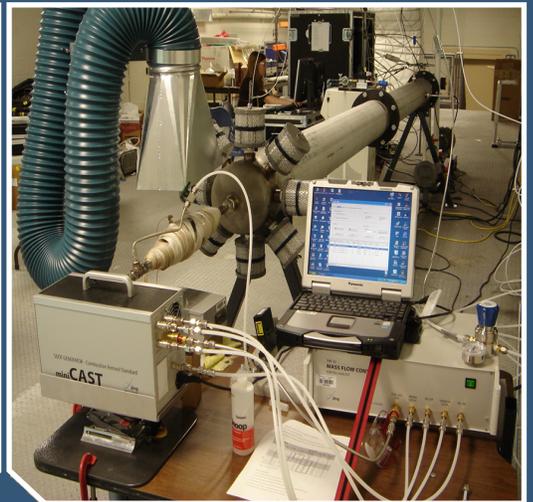


# Laboratory Validation of Four Black Carbon Measurement Methods for Determination of the Nonvolatile Particulate Matter (nvPM) Mass Emissions from Commercial Aircraft Engines



# SCIENCE





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# **Laboratory Validation of Four Black Carbon Measurement Methods for Determination of the Nonvolatile Particulate Matter (nvPM) Mass Emissions from Commercial Aircraft Engines**

## **Final Report**

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# Notice

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## Acronyms and Abbreviations

AAFEX	Aviation Alternate Fuels Experiment
AIR	Aerospace Information Report
APPCD	Air Pollution Prevention and Control Division (EPA)
ARI	Aerodyne Research, Inc.
ARP	Aerospace Recommended Practice
atm	atmosphere(s)
BC	black carbon
$^{\circ}\text{C}$	degree(s) Celsius
C	concentration, also carbon
CBC	concentration black carbon
CC	carbonate carbon
$\text{CH}_4$	methane

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cm	centimeter(s)
CNC	condensation nuclei counter
CO <sub>2</sub>	carbon dioxide
CPC	condensation particle counter
CS	catalytic stripper
DAQ	data acquisition
DAS	data acquisition system
DI	deionized (water)
DMA	differential mobility analyzer
DOC	diesel oxidation catalyst
DQI	data quality indicator
DQO	data quality objective
DR	dilution ratio
EASA	European Aviation Safety Agency
EC	elemental carbon; also electrostatic classifier
EPA	U.S. Environmental Protection Agency
FAA	U.S. Federal Aviation Administration
FID	flame ionization detector
g	gram(s)
GUI	graphical user interface
h	hour(s)
He	helium
HEPA	high-efficiency particulate air
Hz	hertz
IMPROVE	Interagency Monitoring of Protected Visual Environments
I/O	input/output
K	degrees Kelvin
kPa Hg	kilopascal(s) mercury
in.	inch(es)
LED	light-emitting diode
LII	laser-induced incandescence
µg	microgram(s)
µm	micrometer(s)
m	meter(s)
MAAP	multi-angle absorption photometer
mbar	millibar(s)
MBC	mass black carbon
MDL	minimum detection limit

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MFC	mass flow controller
MFM	mass flow meter
mg	milligram(s)
min	minute(s)
mJ	millijoule(s)
mL	milliliter(s)
mm Hg	millimeter(s) mercury
MnO <sub>2</sub>	manganese dioxide
MOP	miscellaneous operating procedure
MSS	Micro Soot Sensor
N <sub>2</sub>	nitrogen
NASA	National Aeronautics and Space Administration
NIOSH	National Institute of Occupational Safety and Health
NIST	National Institute of Standards and Technology
nm	nanometer(s)
NRC	National Research Council–Canada
nvPM	nonvolatile particulate matter
NRMRL	National Risk Management Research Laboratory
OC	organic carbon
OD	outside diameter
PASS	photoacoustic soot sensing
PC	personal computer
PDaq	personal data acquisition (system)
PM	particulate matter
PM <sub>2.5</sub>	fine particles with a diameter of 2.5 μm or less
PPS	primary particle size
psi	pound(s) per square inch
psig	pound(s) per square inch gauge
PTFE	polytetrafluoroethylene
PyC	pyrolytically generated carbon
QAPP	quality assurance project plan
QA	quality assurance
QC	quality control
QFF	quartz-fiber filter
R <sup>2</sup>	correlation coefficient
RMSE	root-mean-square error
RPD	relative percent difference
RSD	relative standard deviation

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s	second(s)
SD	standard deviation
sLpm	standard liter(s) per minute
SMPS	Scanning Mobility Particle Sizer
SOP	standard operating procedure
STP	standard temperature and pressure
T	temperature
$\Delta T$	mean temperature difference or bias
TC	total carbon
TOA	thermal-optical analysis
TOT	thermal-optical transmittance
USB	universal serial bus
UTRC	United Technologies Research Center

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# Executive Summary

Four candidate black carbon (BC) measurement techniques have been identified by the SAE International E-31 Committee for possible use in determining nonvolatile particulate matter (nvPM) mass emissions during commercial aircraft engine certification. These techniques are carbon burn-off, multi-angle absorption photometry (MAAP), laser-induced incandescence (LII), and photoacoustic soot sensing (PASS). This study compared these techniques to the filter gravimetric method while sampling exhaust from a laboratory soot generator (Jing MiniCAST) at five target concentrations ranging from 10 to 1,000  $\mu\text{g}/\text{m}^3$ . At least six replicate tests were conducted at each target concentration using a specially designed flow tunnel system equipped with a single probe and series of sample splitters.

National Institute of Occupational Safety and Health (NIOSH) Method 5040 was selected as the carbon burn-off method for determination of elemental carbon (EC) concentration. The BC instruments evaluated included a modified Thermo Fisher Scientific 5012 MAAP (called the SuperMAAP), Artium Technologies LII 300, and AVL Micro Soot Sensor (MSS) photoacoustic analyzer. All instrument operation followed written procedures established before testing began. A total of 66 test runs were performed in the program during July, August, and September 2011 at the U. S. Environmental Protection Agency's National Risk Management Research Laboratory located in Research Triangle Park, NC, USA.

The following conclusions were reached from the study:

- The measurements made using the four BC measurement methods show a highly linear relationship with increasing particulate matter (PM) concentration in the flow tunnel.
- The four BC measurement techniques were found to be highly correlated with the organic carbon-corrected Teflon reference filter values and with each other for target PM concentrations ranging from 10 to 1000  $\mu\text{g}/\text{m}^3$ . Correlation coefficients ( $R^2$  values) were generally 0.98 or greater depending on test conditions.
- When compared to either the Teflon filter results or NIOSH 5040, the linear regression lines of the data generated by the four techniques were within a maximum of 18 % from perfect agreement (i.e., 1:1 line) for the combined data set.
- Slightly different results were found when the range of target concentrations was limited to 50 to 500  $\mu\text{g}/\text{m}^3$  in the combined data set. A different relationship was also observed for the SuperMAAP and LII within this concentration range, suggesting at least some sensitivity to measured concentration.

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- Due to the high correlations observed among the various methods, there is reason to believe that LII, MSS, and SuperMAAP can provide equivalent results if calibrated against a common BC source.
  - High-quality data were generated in the program with all data quality indicator goals met or exceeded.

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# 1 Introduction

The U. S. Environmental Protection Agency (EPA), U. S. Federal Aviation Administration (FAA), and the European Aviation Safety Agency (EASA) recently requested that the SAE International E-31 Aircraft Emissions Measurement Committee prepare an Aerospace Recommended Practice (ARP) for the determination of nonvolatile particulate matter (nvPM) mass and number emissions from commercial aircraft engines. The three agencies requested that the ARP address both particulate matter (PM) mass and number to support regulatory requirements in both the United States and Europe and to further the efforts of the International Civil Aviation Organization to replace the outdated smoke number standard for new engine certification. In this context, nvPM refers to those particles that exist at engine exit temperature and pressure, consisting mainly of carbonaceous matter (black carbon) from fuel combustion with minor amounts of PM ingested in the engine inlet and metals.

In early 2009, the E-31 Committee prepared Aerospace Information Report (AIR) 6037, which contained extensive information on various candidate PM measurement methods to be used as the starting point for preparation of the ARP for nvPM mass and number (SAE International, 2010). The E-31 PM Subcommittee recognized several black carbon (BC) measurement methods as potentially useful for engine certification as a surrogate for total nvPM mass. For BC mass, carbon burn-off, multi-angle absorption photometry (MAAP), and laser-induced incandescence (LII) were initially identified. More recently, photoacoustic soot sensing (PASS), used in the automotive industry, was identified as a fourth candidate method for use in the ARP. To measure PM number, a condensation nuclei counter (CNC) was chosen as the most suitable technique.

To develop and implement a suitable ARP for nvPM mass and number, each method used for engine certification had to have detailed operation, maintenance, and calibration procedures to standardize the protocol and ensure the quality of the data collected. For PM number, operating and calibration procedures have generally been developed for ground vehicles in Europe. In the case of nvPM mass concentration, however, no such procedures were available. In addition, all four methods identified for the measurement of BC mass are indirect techniques that determine some parameter(s) other than the actual mass in the sample stream. Therefore, a procedure was also needed to relate the output of each method to a National Institute of Standards and Technology (NIST)–traceable direct mass measurement.

Under this project, initiated in spring 2010, standard operating procedures (SOP) were developed for the four PM mass measurement techniques identified by the E-31 Committee to support development of an ARP for nvPM mass. In addition, research was conducted to correlate the output of each method to a NIST-traceable direct mass measurement using the filter gravimetric method.

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Each SOP addresses all aspects of instrument operation, maintenance, and calibration, as well as method quality assurance (QA). Experts in each analytical method were retained to provide critical details for developing the SOPs, and a series of workshops was held to address each instrument type. Upon completion of SOP development, a detailed method validation study was conducted on the four measurement techniques using a system similar to that shown in AIR 6037, Section 11, Technical Annex 1 (SAE International, 2010). This work involved acquiring the instrumentation and an aerosol generator, constructing the experimental system, and performing all necessary calibrations and quality control (QC) checks.

Each candidate measurement method is detailed in Section 2, followed by descriptions of the flow tunnel system and instrumentation (Section 3) and the experimental procedures (Section 4) used in the study. Section 5 provides the experimental results, and Section 6 details the QA/QC employed during testing. Appendices A–K contain the SOPs developed in the program, a modified MAAP method, documentation of instrument calibration, and related information.

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## 2 Candidate Methods

Each of the four BC measurement techniques identified for possible use in aircraft engine certification—carbon burn-off, MAAP, LII, and PASS—is described below. Each method was evaluated and documented, as well as validated against a NIST-traceable filter gravimetric technique.

### 2.1 Carbon Burn-Off Method

In general, the carbon burn-off method uses a laboratory carbon analyzer to determine the total soot mass deposited on a quartz filter by measuring the carbon dioxide (CO<sub>2</sub>) produced while increasing the temperature of the filter in the presence of excess oxygen (O<sub>2</sub>). This method is a quantitative and comparative approach, but is a non-gravimetric technique. However, like the gravimetric analysis of filter samples, the carbon burn-off method requires a minimum mass loading for analysis, which limits its usefulness for “near real time” measurements as would be required in the ARP.

Variations of the carbon burn-off method include National Institute of Occupational Safety and Health Method 5040 (NIOSH, 2003), the Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol (Chow et al., 2001), and the use of commercial thermal carbon analyzers such as the LECO Model RC-412 multiphase carbon/hydrogen/moisture determiner. Of these techniques, only NIOSH 5040 has a recognized, standardized procedure for analysis of quartz filter samples and as such is the method routinely used for source characterization by U.S. EPA’s National Risk Management Research Laboratory (NRMRL) in Research Triangle Park, NC, and other organizations throughout the world. This method was originally developed for determination of organic carbon (OC) and elemental carbon (EC) emissions from diesel-powered vehicles and has been found to be suitable for a wide variety of source categories.

For NIOSH 5040, samples collected on prefired quartz-fiber filters are analyzed using a Sunset Laboratory, Inc. (Tigard, OR, USA) carbon analyzer for determination of OC/EC content. This is a two-stage thermal-optical transmittance (TOT) method with a lower detection limit of approximately 0.2 µg/cm<sup>2</sup> filter area for both OC and EC. In the first stage, organic and carbonate carbon (CC) are evolved in a helium (He) atmosphere as the temperature is stepped to approximately 870 °C. The evolved carbon is catalytically oxidized to CO<sub>2</sub> in a bed of granular manganese dioxide (MnO<sub>2</sub>) and then reduced to methane (CH<sub>4</sub>) in a nitrogen/firebrick “methanator.” CH<sub>4</sub> is subsequently quantified by a flame ionization detector (FID). In the second stage, the oven temperature is reduced, a O<sub>2</sub>-He mix is introduced, and the temperature is stepped

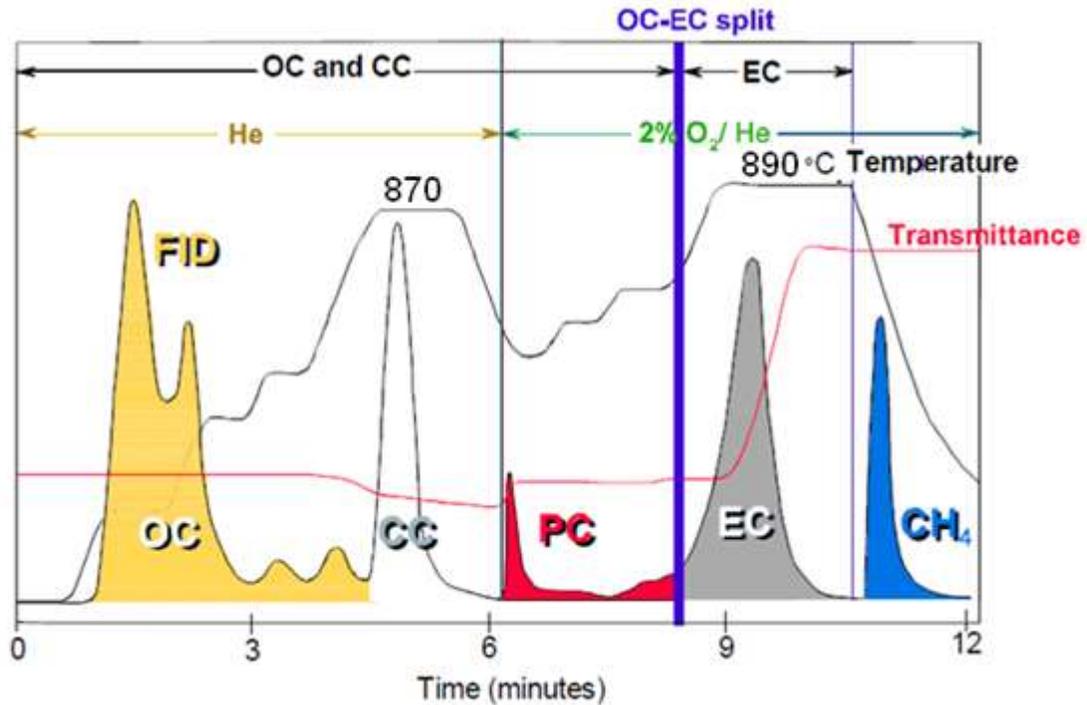
to approximately 890 °C.<sup>1</sup> Details of the NIOSH 5040 temperature program and residence time at each stage are given in Table 2-1.

**Table 2-1. Temperature Profile for the NIOSH 5040 Method Used in this Study**

Carrier Gas	Temperature (°C)	Ramp Rate (°C/s)	Residence Time (s)	Carbon Fraction
He	310	4	70	OC1
He	475	8	60	OC2
He	615	10	60	OC3
He	870	8	105	OC4
98 % He/2 % O <sub>2</sub>	550	9	60	EC1
98 % He/2 % O <sub>2</sub>	625	10	60	EC2
98 % He/2 % O <sub>2</sub>	700	12	60	EC3
98 % He/2 % O <sub>2</sub>	775	13	60	EC4
98 % He/2 % O <sub>2</sub>	890	8	110	EC5
CalibrationOx	1		110	

As O<sub>2</sub> enters the oven, pyrolytically generated carbon (PyC)—carbon evolved between the addition of O<sub>2</sub> and the OC-EC split—is oxidized, causing a concurrent increase in filter transmittance. The split between OC and EC occurs at the point at which the filter transmittance reaches its initial value. Carbon evolved prior to the split is considered OC (including carbonate), and carbon volatilized after the split is considered EC. If the OC-EC split occurs before the addition of O<sub>2</sub>, PyC is zero. Figure 2-1 shows an example thermogram for a filter sample. The split between OC and EC might be inaccurate if the sample transmittance is too low. The EC loading at which this occurs depends on the laser intensity but, in general, is when EC loadings are above 20 µg/cm<sup>2</sup> (NIOSH, 2003).

<sup>1</sup> Note that according to Aerospace Information Report 6037 (SAE International, 2010), the temperature threshold for nvPM is 350 °C. Since the NIOSH method heats the sample far above this temperature, the method could be under-measuring the actual EC mass.



**Figure 2-1.** Thermogram for filter sample containing OC, CC, and EC. PyC is represented here as PC. The final peak is the CH<sub>4</sub> calibration peak. (NIOSH, 2003)

The IMPROVE, or low-temperature, protocol achieves plateaus at 120, 250, 450, and 550 °C in an ultrahigh-purity He atmosphere, remaining at each plateau until a well-defined carbon peak has evolved (Table 2-2). After 2 % O<sub>2</sub> in 98 % He is added at 550 °C, additional carbon evolves, most of which consists of EC and PyC, as indicated by the rapid increase of both the reflectance and transmittance signals. The IMPROVE protocol continues to increase temperatures from 550 °C to 700 °C and then to 800 °C, with the residence time defined by the flattening of carbon signals. The IMPROVE protocol separately reports the carbon evolved for four OC fractions and three EC fractions, while the NIOSH 5040 protocol reports four OC and five EC fractions.

**Table 2-2. Temperature Profile for the IMPROVE Method**

Carrier Gas	Temperature (°C)	Ramp Rate (°C/s) <sup>a</sup>	Residence Time (s) <sup>b</sup>	Carbon Fraction
He	120	1	120	OC1
He	250	2	120	OC2
He	450	3	120	OC3
He	550	4	120	OC4
98 % He/2 % O <sub>2</sub>	550	4	120	EC1
98 % He/2 % O <sub>2</sub>	700	5	120	EC2
98 % He/2 % O <sub>2</sub>	850	6	120	EC3
CalibrationOx	1		110	

<sup>a</sup> Average ramp rate for the IMPROVE protocol is calculated from a residence time of 120 s. To calculate a residence time of 150 s, multiply by 1.25.

<sup>b</sup> Residence time at each temperature in the IMPROVE protocol depends on when the FID signal returns to baseline (minimum is 120 s).

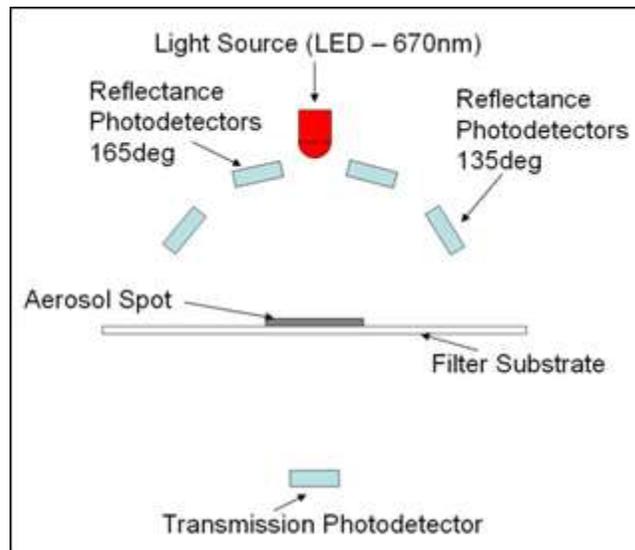
In summary, the NIOSH 5040 and the IMPROVE protocols are similar except that NIOSH OC temperature set points are higher than the temperature set points of IMPROVE. That difference in temperature profile does not influence the total carbon (TC) sampled on the quartz filters. However, the difference in temperatures results in a lower NIOSH EC concentration compared to IMPROVE. The primary reason for this difference is allocation of carbon evolving at the NIOSH 870 °C temperature step in a He atmosphere to the OC rather than the EC fraction (Chow et al., 2001). When this portion of the NIOSH OC is added to the NIOSH EC, the IMPROVE and NIOSH analyses are in good agreement. For both methods, the pyrolysis adjustment to the EC fraction is always higher for transmittance than for reflectance, with transmittance resulting in a lower EC loading (Chow et al., 2001).

EPA NRMRL already had procedures in place for analysis of quartz filter samples per NIOSH 5040 (EPA, 2009a). Modifications were made to that method to provide reproducible procedures for this investigation. However, no protocol existed for the sample collection process required during engine certification. Therefore, a standardized sample collection protocol, similar to that published in 40 CFR Part 86.1065 (EPA, 2012), was written as part of the carbon burn-off SOP, which is discussed in detail in Section 3.

## 2.2 Multi-angle Absorption Photometry

Aerosol absorption photometry analyzes the modification of filter optical properties, such as transmittance or reflectance, caused by the deposition of particles on the filter matrix (Petzold and Schönlinner, 2004). Optical absorption methods are suitable for measuring BC combustion particles because they absorb light very efficiently in the visible spectral range. In addition to its specific sensitivity to BC, aerosol absorption photometry has the further advantage of operating continuously so that time-resolved recording of particle emissions is possible.

The MAAP method determines aerosol light absorption from simultaneous measurements of radiation passing through and scattered back from a particle-loaded fiber filter. The particle-loaded filter is treated as a two-layer system: (1) the aerosol-loaded layer of the filter and (2) the particle-free filter matrix. Radiative processes inside both layers are taken into account separately. Measurements are made at three detection angles to resolve the influence of light-scattering aerosol components on the angular distribution of the back-scattered radiation (Petzold et al., 2002, 2005). Radiation penetrating through the filter is measured at one detection angle,  $\theta = 0^\circ$ , and radiation scattered back from the filter is measured at two detection angles,  $\theta = 135^\circ$  and  $165^\circ$  (Figure 2-2).



**Figure 2-2. Arrangement of the detectors in the MAAP instrument.**

The MAAP method uses the following equation to calculate BC mass loading:

$$MBC = \frac{A (1 - SSA_L) LOD}{\sigma_{abs}}, \quad (2-1)$$

where MBC is the mass of BC deposited on the filter, A is the collection area ( $2 \text{ cm}^2$ ),  $SSA_L$  is the single-scattering albedo of the aerosol-filter layer, LOD is the transmittance or optical depth of the aerosol-loaded filter layer, and  $\sigma_{abs}$  is the specific absorption of BC (assumed constant as  $6.6 \text{ m}^2/\text{g}$  for this instrument). The concentration of BC (CBC; mass per unit volume of air) is then calculated using the following equation:

$$CBC = \Delta MBC / V, \quad (2-2)$$

where  $\Delta MBC$  is the difference in MBC from the previous sample and V is the volume of air sampled between time 1 ( $t_1$ ) and time 2 ( $t_2$ ).

A commercially available instrument based on the MAAP method is offered by Thermo Fisher Scientific (Waltham, MA, USA). The Model 5012 MAAP has been shown to be both robust and

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reliable in several recent field campaigns, including one conducted at Tinker Air Force Base (Howard et al., 2012) and the recent NASA Aviation Alternate Fuels Experiment [AAFEX] (Anderson et al., 2011), and was selected as the method of choice for testing of the Joint Strike Fighter. The Model 5012 has been used by many groups including EPA NRMRL, Aerodyne Research, Inc. (ARI; Billerica, MA, USA), and the United Technologies Research Center (UTRC; East Hartford, CT, USA).

The Model 5012 operates at 670 nm with a time resolution of 1 min. It features automatic filter changing based on absolute transmission, constant sample flow rate (1 m<sup>3</sup>/h) controlled by a variable speed pump, and recording of the actual sample flow, making it an ideal instrument for unattended, long-term monitoring of BC mass loadings in the atmosphere. However, several shortcomings of this MAAP instrument for use in source monitoring applications such as engine certification required modifications to the instrument to allow the following:

- Reducing flow through the filter tape to extend its useful life.
- Isolating the MAAP instrument from the main sampling line during filter changes.
- Calculating BC mass on a 1-Hz basis, logging the data, and providing a graphical user output that can be viewed in real time.
- Calculating the average BC concentrations for the selected sampling periods that will be a function of collected BC mass on the filter and the total air volume sampled.
- Sending commands to the instrument to force a manual filter change.
- Monitoring the transmission percentage in real time so that the operator can determine when a filter change is about to take place.
- Initiating and documenting some type of quality control check to tell the operator the instrument is working properly and ready for use.
- Using an add-on “package” that incorporates all necessary changes for use in certification environments.

The manufacturer (Thermo Fisher Scientific) was not interested in making these modifications due to the low number of MAAP units sold each year. Therefore, independent research was performed in the study to address these issues.

### **2.3 Laser Induced Incandescence**

LII measures the thermal (incandescent light) emission from particles heated by a pulsed laser to temperatures in the 2500 to 4500 K range (Bachalo et al., 2002). LII is a highly selective method that responds only to the presence of BC, making it applicable for measuring the nonvolatile particles produced as a combustion emission because the nonvolatile particles are primarily BC. BC absorbs laser radiation over a broad spectral range and is refractory so that the nanometer-size particles survive heating to the temperatures necessary for the incandescence to be detected.

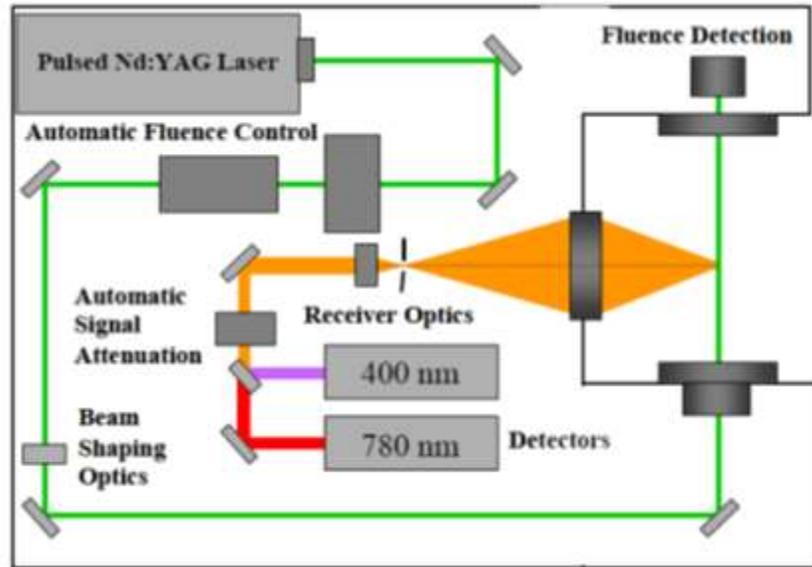
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At these temperatures, all semivolatile organic components that might condense on the BC particles will be evaporated promptly, and most other noncarbonaceous particles will also evaporate or undergo sublimation.

The signals from LII are analyzed to determine mass concentration, volume concentration, active surface area, and primary particle diameter of the particulate emissions. The LII instrument is calibrated by the manufacturer using a known NIST-traceable spectral radiance source. The absolute intensity calibration factors are determined for the instrument-specific optical path (windows, lenses, mirrors, filters, photodetectors). The measurements made with LII are produced with each laser pulse at a rate up to 20 Hz, permitting on-line, time-resolved data collection and reporting of results in real time.

Two extractive LII instruments are currently manufactured that differ in design and operation. Prior to this study, LII has had only limited application to the measurement of aircraft gas turbine emissions, and no SOPs or QC checks are available for either instrument. Therefore, additional research was conducted in this project to mature the LII technology sufficiently for use in engine certification.

The two commercially available LII instruments are the Droplet Measurement Technologies SP2 (Boulder, CO, USA) and the Artium Technologies LII 300 (Sunnyvale, CA, USA). Of the two instruments, the LII 300 (Figure 2-3) offers a greater dynamic range ( $< 0.2$  to  $2 \times 10^6 \mu\text{g}/\text{m}^3$ ) and thus was selected for the present study. The LII 300's novel technique of measuring absolute light intensity theoretically eliminates the need for calibration in a source of soot particles with a known concentration. The absolute intensity method, or self-calibrating LII, applies two-color pyrometry principles centered at 440 and 780 nm to determine the particle temperatures. The LII 300 system consists of a pulsed Nd:YAG laser operating with 60 mJ/pulse at 20 Hz and a wavelength of 1064 nm. EPA NRMRL participated in a study at Wright-Patterson Air Force Base in March 2010 where the LII 300 was shown to be a very promising technique for BC measurement in turbine exhaust.



**Figure 2-3. Schematic layout of the Artium LII 300 system.**  
(Bachalo et al., 2002)

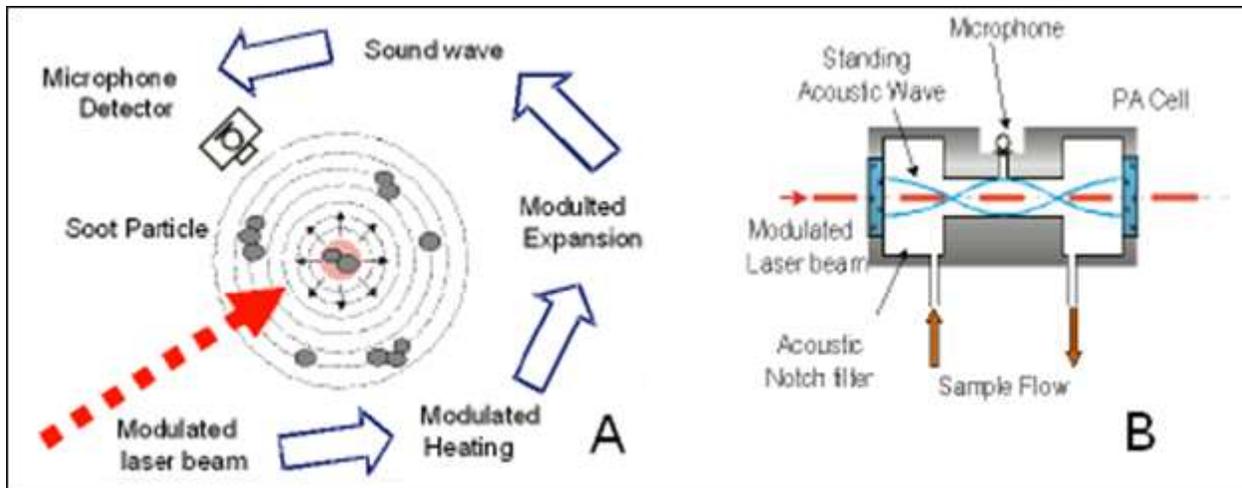
Although the LII 300 was the more applicable of the two instruments available, two remaining issues with the analyzer needed to be resolved before testing:

- Incorporation of a vacuum pump to be able to control and monitor the air sampling flow rate to the instrument.
- Development of an independent QC check to verify proper instrument operation before starting measurement.

Each is described later in this report.

## 2.4 Photoacoustic Soot Sensing

In the photoacoustic measurement method (Figure 2-4A), the sample gas stream containing “black” (i.e., strongly absorbing) soot particulates is exposed to a modulated light beam. When turned on, this light beam heats absorbing particles, which dissipate their heat in the “off” state (Schindler et al., 2004). The resulting pressure fluctuations (expansion and contraction of the carrier gas) are detected by a sensitive microphone. Clean air produces no signal. When the air is loaded with soot or the exhaust gas, the signal rises proportionally to the concentration of soot in the measurement volume. It is possible to measure BC concentrations from  $1$  to  $5 \times 10^4 \mu\text{g}/\text{m}^3$  with this method, which is appropriate to measure the emissions of both diesel and aircraft turbine engines.



**Figure 2-4. Principle of (A) photoacoustic measurement and (B) photoacoustic cell design.**

A simplified setup of a resonant photoacoustic cell is shown in Figure 2-4B (Schindler et al., 2004). The diameter of the cell is small compared to the length, and the diameter is expanded at both ends of the cell (“notch filter”). In this way, a standing acoustic wave is formed, with pressure wave nodes on the ends of the cell and the pressure wave amplitude maximum in the middle. Thus, the microphone is placed in the middle of the resonator. The increase in diameter at both ends reduces the amplitude of the acoustic wave in the notch filter. However, the windows of the measuring cell in the design shown in Figure 2-4B become contaminated. The contamination can be reduced, but not completely eliminated, by allowing the sample gas to flow in from two sides and out from the middle, so the windows must be cleaned periodically.

A commercially available instrument that applies the principles described above is the Model 483 Micro Soot Sensor (MSS) from AVL in Graz, Austria (Schindler et al., 2004). The AVL MSS contains an embedded Class 4 semiconductor laser, which emits radiation at a wavelength of  $808 \pm 5$  nm. Recent testing conducted at Wright-Patterson Air Force Base by EPA NRMRL showed reasonably good correlation of the AVL 483 MSS with both the LII and MAAP instruments.

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## 3 Experimental Apparatus

### 3.1 Experimental System

A specially designed experimental system (Figure 3-1) was constructed by EPA NRMRL and used for all tests conducted during the instrument validation. The system consisted of an aerosol generator, low-speed flow tunnel, and PM mass measurement system. Operation of the system is generally described here with details of each major component provided below. Detailed lists of equipment and software used are provided in Tables 3-1 and 3-2, respectively.

The aerosol generator consisted of a Jing (Bern, Switzerland) Model 5201 (prototype) MiniCAST burner, five mass flow controllers for burner operation, a primary diluter, and a catalytic stripper. Filtered air with a dilution ratio (DR) of 1.4:1 was provided in the primary diluter downstream of the MiniCAST burner, which provided the additional O<sub>2</sub> needed for operation of the catalytic stripper. In the catalytic stripper, a portion of the OC produced by the MiniCAST burner was destroyed by an oxidation catalyst prior to entering the flow tunnel.

At the entrance of the flow tunnel, the diluted aerosol was mixed with the main flow in a region of high turbulence created by the tangential introduction of high-efficiency particulate air (HEPA)-filtered laboratory air through ports located at even distances around the tunnel circumference. This technique provided adequate mixing and low particle losses. Downstream of the aerosol injection point, a sample was collected through a 165-cm-long straight-through extraction probe whose entrance was located 20 tunnel diameters downstream and four diameters upstream of any flow disturbance. The probe was connected to the instrument suite, which consisted of a PM<sub>2.5</sub> cyclone preseparator, short transfer line, and a series of 2 two-way flow splitters followed by a four-way splitter that was used to provide a split aerosol sample to each of the four candidate instruments plus the Teflon filter reference sampler (Figure 3-2). Downstream of the four-way splitter, identical 314-cm-long transfer lines provided the split sample to the four instruments to maintain consistent particle losses in the lines. A filtered bypass and pneumatically operated three-way valve also were installed between the tunnel exit and splitters to allow all analyzers to sample either filtered laboratory air or MiniCAST exhaust. The rest of the effluent from the flow tunnel was removed from the laboratory via the building ventilation system using either of two blowers provided with the system or, for the highest concentration measurements, a vacuum pump.

The primary instrumentation suite consisting of the four candidate measurement methods was supplemented by an independent “process” monitor, a TSI 3936 Scanning Mobility Particle Sizer (SMPS), to determine PM number concentrations as well as size distribution. The SMPS was used only to monitor MiniCAST burner operation during testing and thus was not included in the instrument evaluation *per se*.

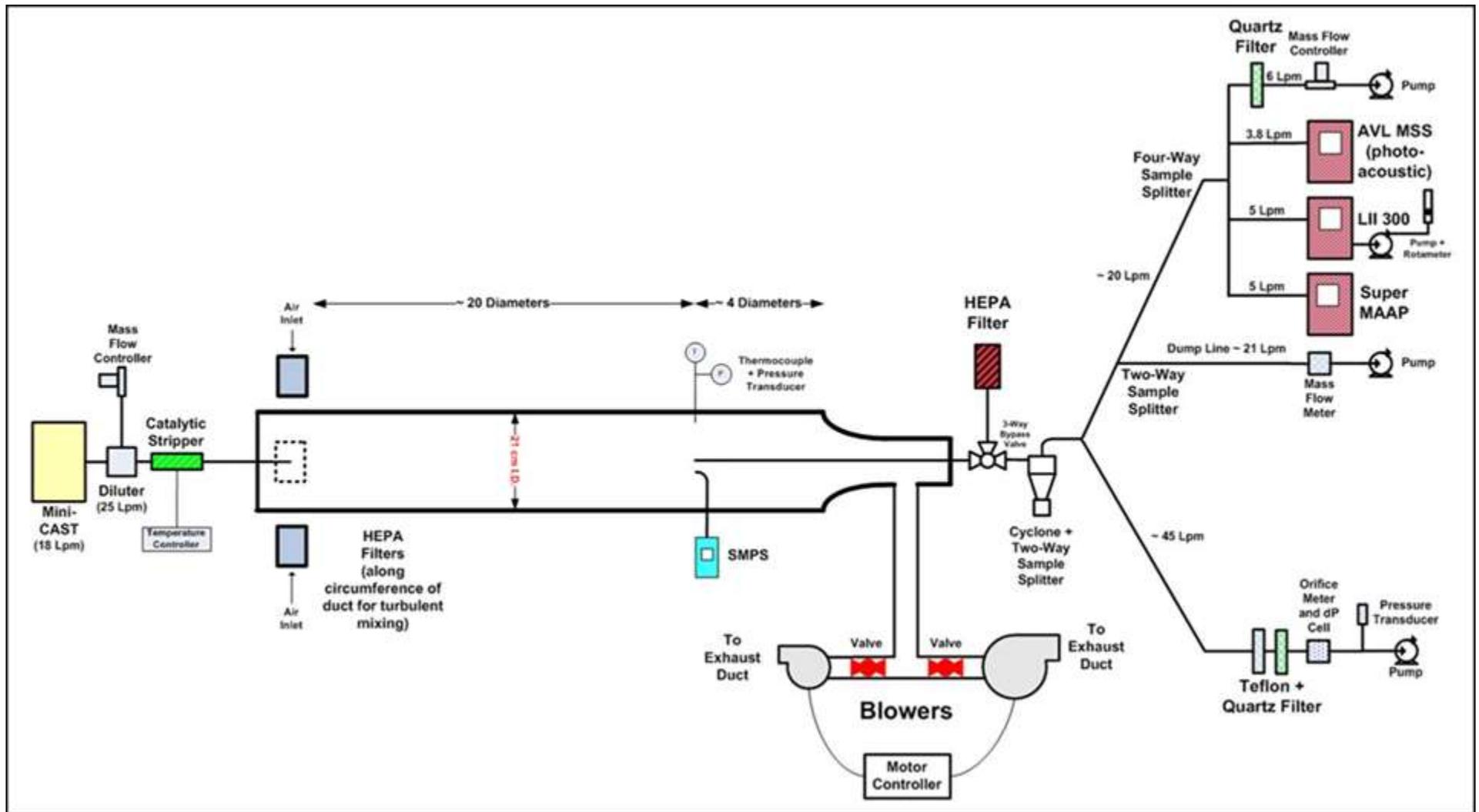


Figure 3-1. Flow tunnel and associated measurement system

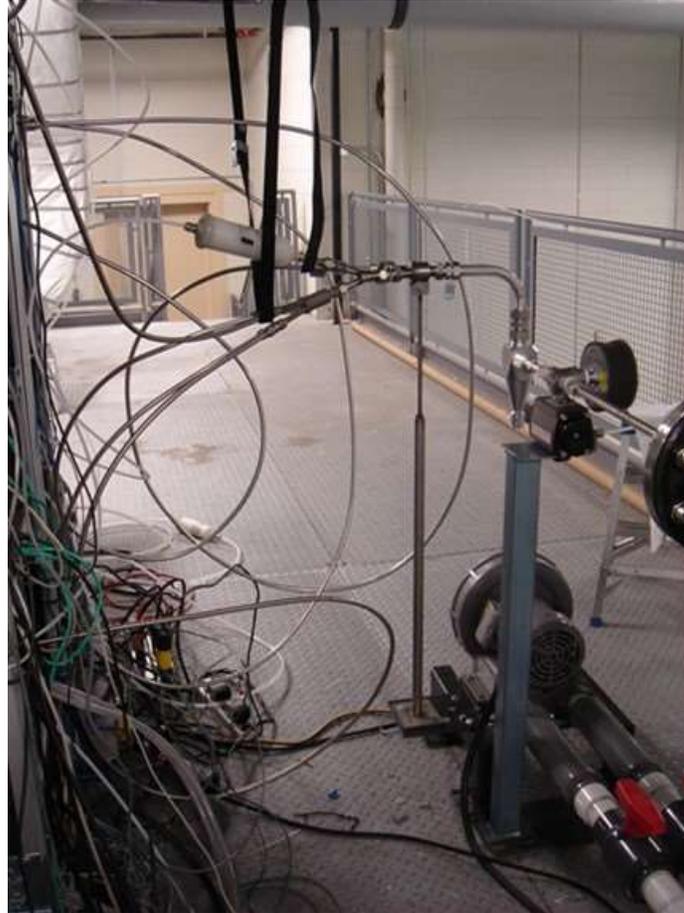
**Table 3-1. Instruments and Equipment**

Name	Abbreviation	Model Number	Supplier	Location in Tunnel System
Soot generator	MiniCAST or CAST	5201 MiniCAST Prototype	Jing Ltd., Bern, Switzerland	Tunnel inlet
Mass flow controller (MFC) system for soot generator	MFC box	F-42	Jing Ltd., Bern, Switzerland	Tunnel inlet
Catalytic stripper (CS) with temperature controller	CS	NA	Southwest Research Institute, San Antonio, TX, USA	Downstream of MiniCAST at tunnel inlet
Multi-angle absorption photometer	SuperMAAP	Modified 5012 MAAP	Thermo Fisher Scientific, Waltham, MA, USA	Instrument suite
Laser-induced incandescence instrument with laser power supply	LII 300	LII 300 + ICE 450	Artium Technology, Inc., Sunnyvale, CA, USA	Instrument suite
Micro Soot Sensor with conditioning unit	MSS 483	AVL MSS 488 + AVL conditioning unit	AVL, Graz, Austria	Instrument suite
Scanning Mobility Particle Sizer	SMPS	3081 differential mobility analyzer (DMA) + 3025A condensation particle counter (CPC)	TSI, Shoreview, MN, USA	Tunnel sampling port
Thermal-optical carbon analyzer	OC/EC analyzer	Dual-optical carbon analyzer	Sunset Laboratory, Tigard, OR, USA	NA
Analytical microbalance	Microbalance	Sartorius ME5	Sartorius-North America, Elk Grove, IL, USA	NA
Laboratory transducer – low pressure	Orifice meter differential pressure (dP) cell	PX653-10D5V	Omega Engineering, Stamford, CT, USA	Teflon filter sampler
Air-actuated bypass valve	Air switch valve	SR63 – 530163	Industrial Automation Components, London, Canada	Three-way switching valve upstream of cyclone
Pressure transducer	PT – sample line	PX309-015A5V	Omega Engineering, Stamford, CT, USA	Teflon filter sampler
Pressure transducer	PT – tunnel line	PX309-015A5V	Omega Engineering, Stamford, CT, USA	Tunnel sampling port
PM <sub>2.5</sub> cyclone	Cyclone	URG-2000-30EC	URG Corporation, Chapel Hill, NC, USA	Between switching valve and flow splitters
Personal Data Acquisition System	PDAQ	PDAQ/56	Measurement Computing Corporation, Norton, MA, USA (now National Instruments, Austin, TX, USA)	Two pressure transducers, tunnel temperature, primary diluter mass flow meter (MFM), dump line MFM, quartz filter sampler MFC, Teflon filter sampler dP cell pressure transducer

Name	Abbreviation	Model Number	Supplier	Location in Tunnel System
MFM 0–50 sLpm nitrogen (N <sub>2</sub> )	MFM – dilution air	FMA 1700/1800	Omega Engineering, Stamford, CT, USA	Primary diluter downstream of MiniCAST
MFM 0–50 sLpm N <sub>2</sub>	MFM – dump line	FMA 1700/1800	Omega Engineering, Stamford, CT, USA	Dump line off first two-way flow splitter
MFC 0–50 sLpm	MFC – quartz-fiber filter (QFF) line	GFC-1133	Dwyer Instruments Inc, Niagara Falls, NY, USA	Quartz filter sampler
Ring compressor	Big blower	VFC400A-7W	Fuji Electric, Japan	Main tunnel flow
Ring compressor	Small blower	VFC200A-7W	Fuji Electric, Japan	Main tunnel flow
Vacuum pump	Pump – QFF line	0523-101Q-Q582DX	Gast MFG Corp., Benton Harbor, MI, USA	Quartz filter sampler
Vacuum pump	Pump – dump line	0523-V103-G18DX	Gast MFG Corp., Benton Harbor, MI, USA	Dump line from first two-way flow splitter
Vacuum pump	Pump – Teflon filter line	2807CE72J	Rietschie Thomas, Sheboygan, WI, USA	Teflon filter sampler
Vacuum pump	Pump for 1000 µg/m <sup>3</sup>	2807CE72J	Rietschie Thomas, Sheboygan, WI, USA	Main tunnel flow
Vacuum pump	Pump for LII	2107CA20 C	Rietschie Thomas, Sheboygan, WI, USA	LII 300

**Table 3-2. Software/Firmware**

Instrument/Device	Firmware Version	Software Version	Software/Firmware Manufacturer
MiniCAST + MFC box	NA	Get Red-y	Vögtlin Instruments AG, Aesch, Switzerland
Modified MAAP	V1.29	V1.3 (Custom)	Thermo Fisher Scientific, Waltham, MA, USA and National Instruments Corp, Austin, TX, USA (LabView)
LII 300	IP.192.168.1.110	AIMS 3.8	Artium Technologies, Sunnyvale, CA, USA
AVL 488	2.0	1.1.0.5	AVL, Graz, Austria
PDaq	NA	DasyLab 10.00.01	National Instruments Corp, Austin, TX, USA
SMPS	2.11	AIM 9.0.0.0	TSI Inc., Shoreview, MN, USA



**Figure 3-2. Sample distribution system to instruments.**  
Except for the cyclone, all components are made of stainless steel.

## **3.2 Aerosol Generator System**

### **3.2.1 *MiniCAST 5201 and Primary Diluter***

A Jing MiniCAST Model 5201 prototype<sup>2</sup> (Figure 3-3), used as the soot generating device, produces an aerosol of carbonaceous particles of adjustable and repeatable size and chemical composition. As a soot source, the MiniCAST uses a propane diffusion flame, in which soot particles are formed during pyrolysis of the fuel. To generate the soot particles, the oxidation air supply was kept below stoichiometric limits. Consequently particles contained within the exhaust gases arose out of the flame and left the combustion chamber. The particle stream was then mixed with quenching gas (N<sub>2</sub>) to prevent further combustion and to stabilize the soot particles.

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<sup>2</sup> Note that this is a standard Model 5201 device specifically modified by the manufacturer (Jing) at EPA's request to produce a slight positive pressure at the outlet of the unit. It was known before starting the study that the MiniCAST does not produce a soot aerosol representative of aircraft turbines. It was, however, the best commercially available laboratory soot generator suitable for use in the study.

This quenching inhibits condensation when the particle stream escapes from the flame to the ambient air. Subsequently, an axial flow of dilution air was supplied to reduce the concentration of the particle stream prior to exiting the MiniCAST. Operation of the MiniCAST, together with the different gas flows, is illustrated in Figure 3-3; the experimental setup is shown in Figure 3-4.

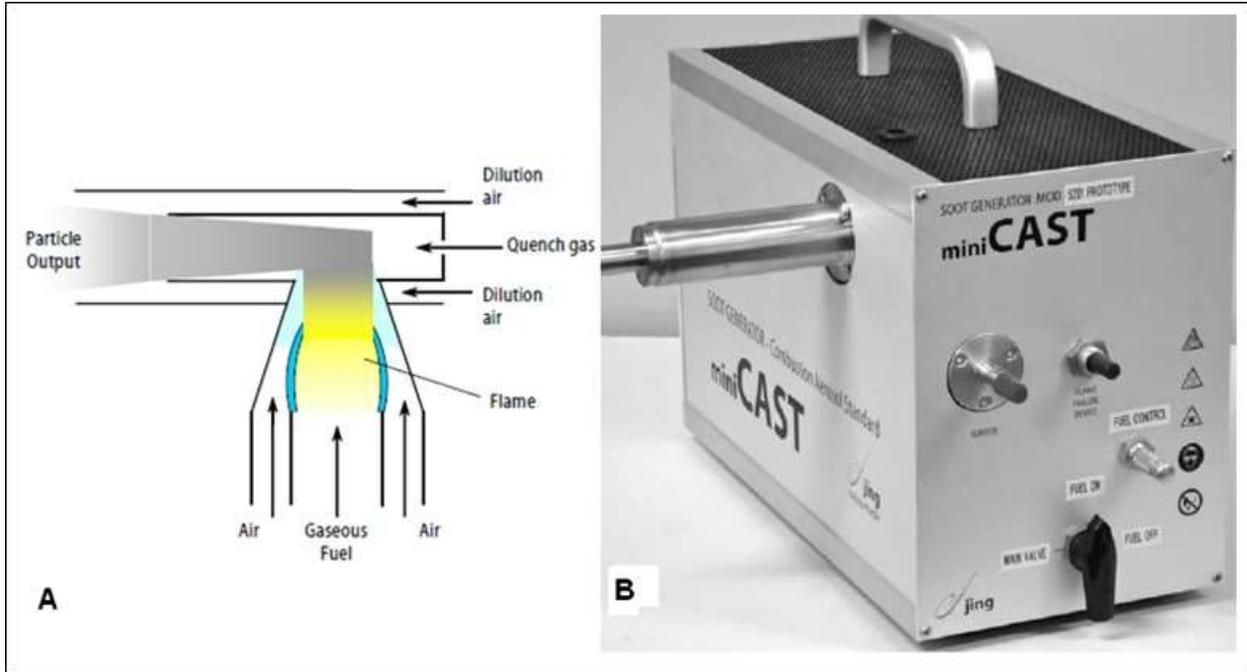


Figure 3-3. (A) Operation principle of the MiniCAST burner and (B) front view of the MiniCAST prototype used for this study.



Figure 3-4. MiniCAST, primary diluter, and catalytic stripper installed on the flow tunnel.

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The MiniCAST flame supplies soot particles at high concentration ( $10^7$ – $10^9$  particles/cm<sup>3</sup>), which are diluted for different applications. The state of the flame and the features of the generated soot particles primarily result from the flow settings. By varying the flow settings, the particle size can be adjusted in a range of 20 to 200 nm (mean electrical mobility particle diameter). In addition, the OC/EC ratio varies with operational set point. The equivalence ratio and the flow of mixing nitrogen gas are the most important parameters responsible for formation of particles of different sizes. The rich flames (higher propane/air ratio) result in a high proportion of OC and small particle sizes. A lean flame (lower propane/air ratio) results in less OC and more EC and generally larger particle sizes. Thus, for the higher EC content desired in the current work, lean flames were more favorable and thus used in the study.

In addition to the burner itself, a Model PMF-42 MFC unit (on loan from the National Research Council [NRC]–Canada) was used in order to control five flow settings: fuel (propane), oxidation air, mixing gas (N<sub>2</sub>), quenching gas (N<sub>2</sub>), and dilution air. The unit consists of five gas flow controllers (Red-y Smart series, Vögtlin Instruments, Aesch, Switzerland). The Get Red-y software package provided by the manufacturer is used to control, change, and log the operating parameters of these five units. All MFCs were calibrated by the EPA NRMRL Air Pollution Prevention and Control Division (APPCD) Metrology Laboratory prior to use according to miscellaneous operating procedure (MOP) FV-0201.1 (EPA, 2009b).<sup>3</sup> Detailed instructions on operating the MiniCAST and PMF-42 control unit, together with the control PC software, are provided in SOP 2101 in Appendix A.

In the present study, the soot aerosol exiting the MiniCAST was diluted (DR = 1.4) with HEPA-filtered compressed air before it reached the catalytic stripper (CS). The dilution flow was measured using an Omega Engineering Model FMA 1700/1800 MFM. The total flow entering the CS was approximately 43 L/min (~ 18 L/min from MiniCAST plus 25 L/min dilution air). To test the selectivity of each candidate instrument/method, the same experiments (same concentration conditions) were performed both with and without the CS in operation.

### **3.2.2 Catalytic Stripper**

The purpose of the CS was to remove the semivolatile (typically OC) fraction by passing raw or diluted exhaust over an oxidation catalyst heated to 300 °C. The CS consisted of a heated platinum oxidation catalyst, a temperature probe at the inlet and outlet, heating elements, and a temperature controller capable of maintaining 300 °C (Figure 3-5). The oxidation catalyst used is a commercially available diesel oxidation catalyst (DOC; Clariant SE, Munich, Germany) designed to remove volatile hydrocarbons from diesel exhaust by oxidizing the volatile hydrocarbon species to CO<sub>2</sub> and H<sub>2</sub>O. The catalyst and geometry of the substrate were characterized and sized to minimize solid particle losses in the size range typical of diesel

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<sup>3</sup> Note that all SOPs and MOPs are either appended or can be found at the internal APPCD SharePoint site. SOPs are generally developed for major equipment used in the study and MOPs are for ancillary equipment.

exhaust and theoretically to achieve near complete removal of volatile material (Khalek, 2007). The DOC was insulated and equipped for heating up to 400 °C, as shown in Figure 3-5.

The CS, provided to EPA by Southwest Research Institute, had a stainless steel enclosure and conical (12.5°) inlet and outlet with 9.5-mm inlet and outlet outside diameter connections (Khalek, 2007; Khalek and Bougher, 2011). The CS is sized for a flow rate of 0.025 sLpm through each channel of the catalyst. Detailed properties and dimensions of the DOC are provided in Table 3-3.



**Figure 3-5. Components of the catalytic stripper system.**

**Table 3-3. DOC Properties and Dimensions Used in the Catalytic Stripper**

DOC Component	Property/Dimensions
Material	Ceramic monolith
Wash coat	Zeolite, alumina
Catalyst	Platinum
Geometry	Square channel
Overall length (cm)	~ 7.5
Overall diameter (cm)	~ 7.5
Cell density (number of cells per cm <sup>2</sup> )	54.2
Square channel wall thickness (cm)	0.0139
Square channel length (cm)	~ 7.5
Square channel open width or height (cm)	0.127

### 3.3 Instrumentation Suite

As described in Section 2, four candidate methods were tested in the study:

- Carbon burn-off method (NIOSH 5040) with laboratory thermal-optical carbon analyzer from Sunset Laboratory, Inc.
- Multi-angle absorption photometry with the modified 5012 MAAP instrument from Thermo Fisher Scientific Corporation.
- Laser-induced incandescence with the LII 300 instrument from Artium Technologies.
- Photoacoustic soot sensing with the MSS 483 from AVL.

The four candidate methods are described briefly in the following sections. SOPs for each instrument and documentation of development of an improved MAAP method (SuperMAAP) can be found in Appendices B through F.

#### 3.3.1 Thermal-Optical Carbon Analyzer

Samples were collected on 47-mm quartz-fiber filters (QFFs) that were pre-fired at 550 °C for 12 h before sampling and stored in a freezer at a nominal temperature of -20 °C. Upon completion of each experiment, the QFF samples were analyzed using a Sunset Laboratory TOT carbon analyzer that simultaneously measures transmission and reflectance signals. A schematic diagram of the Sunset Laboratory analyzer is shown in Figure 3-6. Details for collection and analysis of the quartz filter samples are provided in SOP 2104 available in Appendix B.

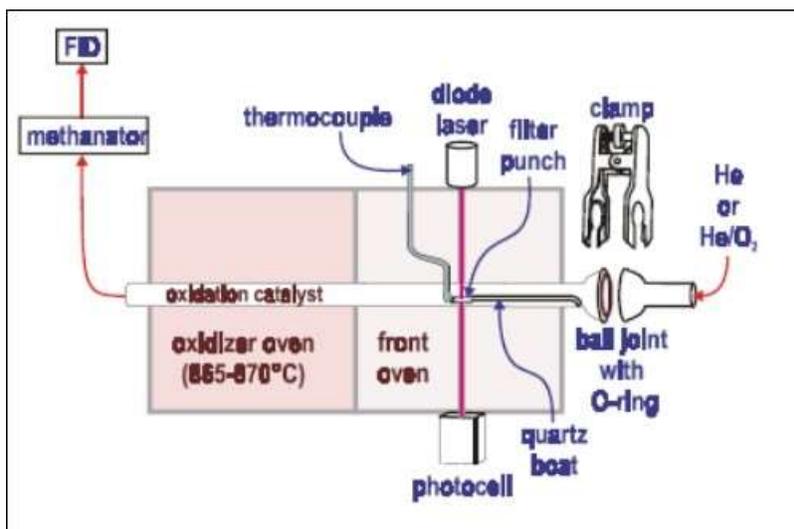


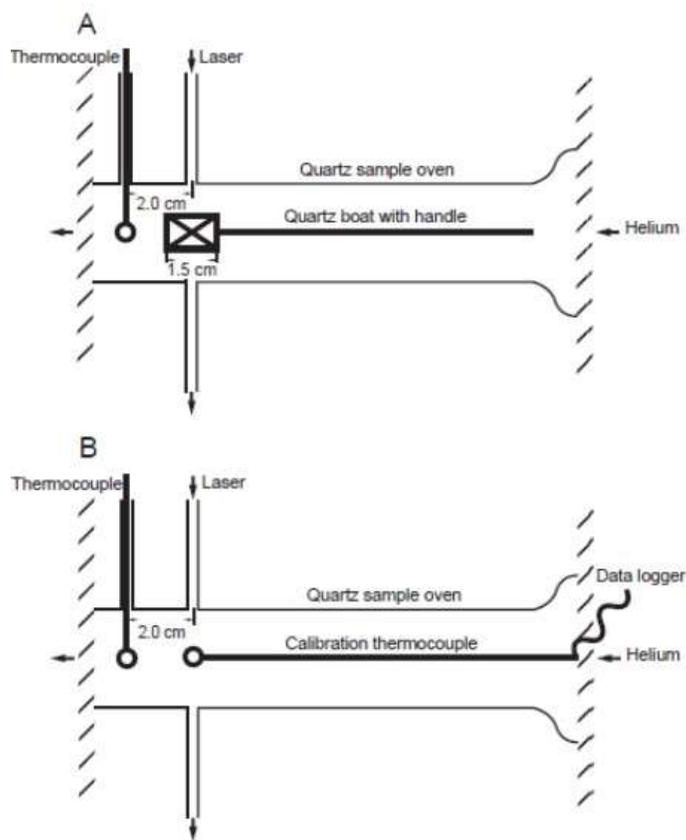
Figure 3-6. Sunset Laboratory thermal-optical carbon analyzer.

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During analysis, a 1.5 cm<sup>2</sup> punch from the exposed filter is placed in a quartz boat and positioned in the path of a red-light diode laser that is used to monitor transmittance of the filter and to determine the OC/EC split time. An internal thermocouple at the end of the boat is used to monitor the sample temperature during the analysis. All carbon species evolved from the filter are converted to CO<sub>2</sub> in the oxidation oven, and then the CO<sub>2</sub> is catalytically reduced to CH<sub>4</sub> before being measured by an FID. Before starting sample analysis for the present project, the MFCs used to control delivery of gases to the Sunset analyzer were calibrated using a Gilibrator system (Zefon International, Ocala, FL, USA) by the APPCD Metrology Laboratory using MOP FV-0237.0 (EPA, 2010).

In addition to MFC calibration, studies performed by Phuah et al. (2009) and Chow et al. (2005) showed that the sample (filter) temperature and the temperature measured by the thermocouple can differ by 10 to 50 °C. Since temperature precision in thermal-optical analysis (TOA) is required for accurate measurements, Sunset Laboratory developed a temperature calibration procedure that was performed on the instrument used in this study before starting the measurements (Pavlovic et al., 2014).

Sunset Laboratory provided the temperature calibration kit, which is designed to satisfy QA/QC requirements, increase reliability of carbon results, and improve inter-instrument comparisons. The calibration kit consists of a serial temperature data acquisition unit (precision ± 0.3 °C for the -80–500 °C temperature range and ± 0.55 °C for the 500–1350 °C range [Model MDSi8, Omega Engineering, Stamford, CT, USA]), NIST-traceable thermocouple (Inconel-shielded K-type thermocouple certified for high temperatures [Omega Engineering Calibration Report # OM-110802626] with 1/16-in. sheath diameter, and front oven interface hardware. Thermocouple-produced temperature data were recorded at a frequency of 1 Hz and with 0.1 °C resolution. For calibration, the quartz boat with quartz filter (Figure 3-7A) used during normal TOA were replaced with the front oven interface hardware outfitted with the NIST-traceable thermocouple (Figure 3-7B).



**Figure 3-7. The (A) sample analysis set and (B) calibration set of the Sunset Laboratory carbon analyzer.**

(Note the position of the oven temperature sensor relative to the filter sample.)

The tip of the oven calibration thermocouple was positioned where the center of the quartz filter typically resides during TOA operation, which is approximately 2 cm upstream of the thermocouple used to monitor the oven temperature (Figure 3-7). This position also happens to be where the laser beam ( $\lambda = 632.8 \text{ nm}$ ) used to monitor pyrolysis passes through the filter. For the sake of comparison, oven calibrations were performed using both the NIOSH 5040 and IMPROVE temperature operating conditions. Details about residence time and temperature ramp rate set points for the NIOSH 5040 protocol can be found in Khan et al. (2012). For calibration using the IMPROVE protocol, the residence time at each temperature step was 120 s.

Two temperatures were recorded during the oven calibration routine:  $T_{\text{OVEN}}$  as measured by the built-in oven temperature sensor and  $T_{\text{FILTER}}$  as measured by the calibration kit. Both temperatures were recorded when the readings for the sample oven ( $T_{\text{OVEN}}$ ) were stable at each set-point temperature ( $T_{\text{SETPOINT}}$ ) required by the NIOSH 5040 and IMPROVE protocols for each temperature step. Before calibration,  $T_{\text{SETPOINT}} = T_{\text{OVEN}}$ . However, previous studies such as Phuah et al. (2009) showed that  $T_{\text{FILTER}} \neq T_{\text{SETPOINT}}$  and therefore  $T_{\text{FILTER}} \neq T_{\text{OVEN}}$ . Differences among  $T_{\text{SETPOINT}}$ ,  $T_{\text{OVEN}}$ , and  $T_{\text{FILTER}}$  were determined, and temperature coefficients

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(approximately equal to temperature biases measured) in the instrument control software parameter files were adjusted so that  $T_{\text{FILTER}} = T_{\text{SETPOINT}}$ . In other words, coefficient values were adjusted to force the temperature at the sample oven thermocouple ( $T_{\text{OVEN}}$ ) to reflect the value required to achieve  $T_{\text{SETPOINT}}$  at the filter because  $T_{\text{OVEN}} \neq T_{\text{FILTER}}$  either before or after the calibration. For each TOA method (NIOSH 5040 and IMPROVE), the oven calibration procedure was performed in triplicate with the calibration unit removed and then replaced for each trial. This calibration was accomplished before adjustment of the temperature coefficients. After the coefficients were adjusted in the software, the calibration/checking procedure was performed again in triplicate to measure and record  $T_{\text{FILTER}}$  during each temperature step required by the NIOSH 5040 and IMPROVE methods to ensure  $T_{\text{FILTER}} = T_{\text{SETPOINT}}$  and full compliance with the method.

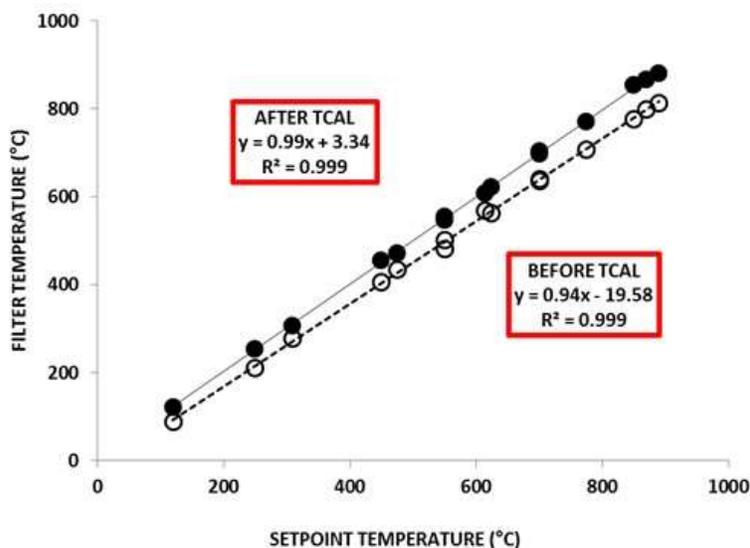
All temperatures reported here as  $T_{\text{FILTER}}$  (measured by the calibration thermocouple) represent the temperatures measured in the center of the filter, while in practice there will be gradients across the filter. In addition, the quartz boat with filter used during normal instrument operation compared with the calibration thermocouple might experience different heating rates inside the front oven of the instrument, given that the heat capacity of the contents inside the oven is different. However, this study focused on the temperatures recorded only when they reached steady state for each temperature step. The assumption for this study was that the steady-state temperature of the quartz boat with filter inside the front oven will be the same as the steady-state temperature recorded during calibration with the thermocouple.

Table 3-4 summarizes temperatures required ( $T_{\text{SETPOINT}}$ ) at each programmed step and the average  $T_{\text{FILTER}}$  measured by the calibration kit, along with the average temperature deviations (% difference) for the dual-optics analyzer tested as part of the current study.  $T_{\text{FILTER}}$  values were systematically lower than  $T_{\text{SETPOINT}}$  values prior to calibration over the entire temperature range evaluated for both TOA protocols. This was presumably due to (1) the unique location of each thermocouple as shown previously in Figure 3-7 and (2) a different allocation of heating coils around the sample boat and in the sample oven. Phuah et al. (2009) attributed the lower  $T_{\text{FILTER}}$  temperatures to the less tightly packed heating coils around the quartz tube where the transmittance laser passes compared to the tightly packed heating coils in the sample oven. These existing instrument limitations most likely resulted in mean temperature difference or bias ( $\Delta T$ ) between  $T_{\text{SETPOINT}}$  and  $T_{\text{FILTER}}$  measured in this study between 32 °C and 75 °C. The  $\Delta T$  observed is less at low temperatures ( $\leq 43$  °C for temperatures  $\leq 450$  °C) than at high temperatures ( $\leq 75$  °C for temperatures  $\leq 890$  °C). The  $\Delta T$  under the NIOSH and IMPROVE protocols varied at the  $T_{\text{SETPOINT}}$  of 550 °C. Inherent in the NIOSH temperature protocol was a higher  $\Delta T$  (70 °C) at the He-O<sub>2</sub> introduction step where temperature decreases from 870 °C to 550 °C. The high  $\Delta T$  at that step is presumably due to the wide temperature gap (870 °C to 550 °C) and short residence time.

**Table 3-4. Filter Temperatures Measured before Calibration for NIOSH 5040 and IMPROVE Protocol**

Carbon Fraction	NIOSH 5040			IMPROVE		
	T <sub>SETPOINT</sub> (°C)	T <sub>FILTER</sub> (°C)	ΔT °C (% difference)	T <sub>SETPOINT</sub> (°C)	T <sub>FILTER</sub> (°C)	ΔT °C (% difference)
OC1	310	278	32 (10)	120	88	32 (27)
OC2	475	435	40 (8)	250	211	39 (16)
OC3	615	569	46 (7)	450	407	43 (10)
OC4	870	800	70 (8)	550	501	49 (9)
EC1	550	482	68 (12)	550	501	49 (9)
EC2	625	563	62 (10)	700	639	61 (9)
EC3	700	637	63 (9)	850	777	73 (9)
EC4	775	707	68 (9)			
EC5	890	813	75 (8)			

Consistent with our findings, Phuah et al. (2009) observed ΔT values of 35–85 °C that varied with each Sunset Laboratory instrument, while Chow et al. (2005) found that ΔT depended on the temperature ramp. Chow et al. (2005) did not observe a linear correlation between T<sub>FILTER</sub> and T<sub>SETPOINT</sub>, although Phuah et al. (2009) and the present study do indicate such a correlation. Figure 3-8 shows that the T<sub>FILTER</sub> and T<sub>SETPOINT</sub> relationship is linear based on temperature data obtained at nine NIOSH and six IMPROVE temperatures that precede calibration. Regression analysis shows the slope approaching unity (0.94 ± 0.01) but lower than the values measured on four other Sunset Laboratory instruments found by Phuah et al. (2009). A regression correlation ( $r = 1.000$ ;  $R^2 = 0.999$ ) suggests that the T<sub>SETPOINT</sub> can be increased systematically until T<sub>FILTER</sub> = T<sub>SETPOINT</sub> and T<sub>FILTER</sub> meets the T<sub>SETPOINT</sub> requirements of the NIOSH and IMPROVE protocols.



**Figure 3-8. Linear regression results before and after temperature calibration.**

Following oven calibration,  $T_{\text{FILTER}}$  was within 1 % and 1.7 % of  $T_{\text{SETPOINT}}$  for the NIOSH and IMPROVE protocols, respectively (Table 3-5). The  $\Delta T$  at temperatures below 450 °C was  $\leq 5$  °C as compared with  $\Delta T \leq 43$  °C before calibration (TCAL). At temperatures of 550 °C - 890 °C,  $\Delta T$  was  $\leq 9$  °C compared with  $\Delta T \leq 75$  °C before TCAL. The  $T_{\text{FILTER}}$  and  $T_{\text{SETPOINT}}$  linear relationship after calibration is also shown in Figure 3-8. A higher regression slope ( $0.99 \pm 0.01$ ) and a significantly lower intercept ( $3.34 \pm 3.05$ ) confirm the effectiveness of the temperature calibration.

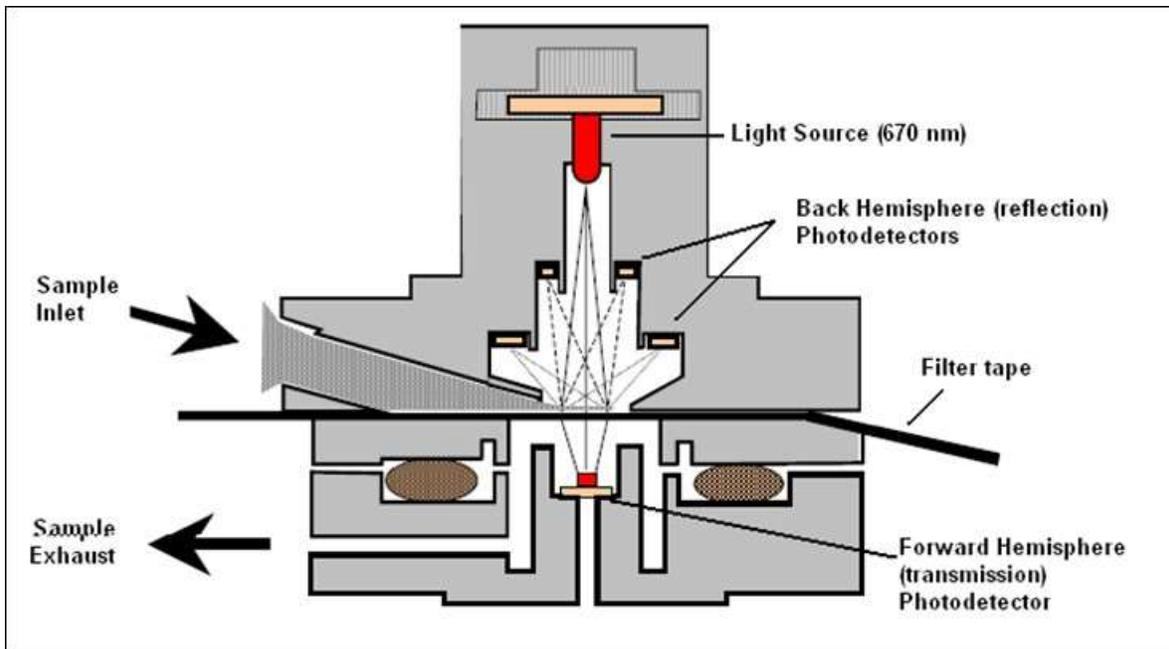
**Table 3-5. Filter Temperatures Measured after Calibration and Software Adjustments**

Carbon Fraction	NIOSH 5040			IMPROVE		
	$T_{\text{SETPOINT}}$ (°C); $r^*$	$T_{\text{FILTER}}$ (°C)	$\Delta T$ °C (% difference)	$T_{\text{SETPOINT}}$ (°C); $r^*$	$T_{\text{FILTER}}$ (°C)	$\Delta T$ °C (% difference)
OC1	310; 24	307	3 (1.0)	120; 48	122	2 (1.7)
OC2	475; 28	472	3 (0.6)	250; 39	254	4 (1.6)
OC3	615; 40	609	6 (1.0)	450; 42	455	5 (1.1)
OC4	870; 65	866	4 (0.5)	550; 50	555	5 (0.9)
EC1	550; 61	546	4 (0.7)	550; 50	555	5 (0.9)
EC2	625; 54	622	3 (0.5)	700; 61	703	3 (0.4)
EC3	700; 56	697	3 (0.4)	850; 74	854	4 (0.5)
EC4	775; 61	772	3 (0.4)			
EC5	890; 71	881	9 (1.0)			

\*Temperature correction coefficients implemented in the software parameter files.

### 3.3.2 SuperMAAP

As described in Section 2, the Thermo Fisher Scientific 5012 MAAP measures ambient BC concentrations and aerosol light absorption properties. The design of the MAAP detection chamber is illustrated in Figure 3-9. The aerosol sample is drawn into the instrument through the inlet. The sample flows through the down tube and deposits onto the glass-fiber filter tape. The filter tape accumulates an aerosol sample up to a threshold transmission value (nominally 20 % transmission), whereupon the filter tape automatically advances before reaching saturation. Within the detection chamber, a 670-nm visible light source is aimed toward the deposited aerosol and filter tape matrix. The light transmitted into the forward hemisphere is reflected into the back hemisphere and measured by a series of photodetectors. During sample accumulation, the light beam is attenuated from an initial reflectance reading from a clean filter spot. The reduction of light transmission, multiple reflectance intensities, and air sample volume are continuously integrated over the sample run to provide 1-min data output of BC concentration measurements.



**Figure 3-9. Diagram of 5012 MAAP detection chamber.**

To fulfill the requirements of the present study, the 5012 MAAP was substantially modified to produce the “SuperMAAP” as follows:<sup>4</sup>

- Flow was reduced through the filter tape to extend its useful life. Sample flow was software controlled and consisted of a total aerosol flow that entered the inlet of the instrument and a sample flow that was directed through the filter tape. The BC concentration was calculated as the mass of BC collected on the tape during the analysis per volume of sample passed through the tape.
- Software was available to collect and process BC concentration data on a 1-Hz basis. This information was stored in a “raw” data file that included all output parameters from the instrument plus the MBC and CBC.
- Average BC concentrations were calculated at the end of a run along with the standard deviation (SD) of the measurement using a linear regression approach. The average values were stored in a “processed” data file.
- The SuperMAAP was automatically isolated from the main sampling line during the filter changes, providing an unassisted zero check.
- A command could be sent to the instrument to force a manual filter change anytime during the experiment.

<sup>4</sup> EPA NRMRL staff involved in this work included Mr. William Mitchell and Mr. William Squire.

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- The new software monitored the percent transmission in real time so that the operator could determine when a filter change was about to take place.
  - A documented QC check was established to tell the operator if the instrument was working properly and ready for use.
  - An add-on “package” incorporating the necessary changes was developed by EPA NRMRL for use in certification environments.

Figure 3-10 depicts the SuperMAAP configuration, which consists of the standard 5012 MAAP instrument (lower box) plus the new hardware components installed in a separate enclosure on top. Before use, both SuperMAAP MFCs were calibrated by the APPCD Metrology Laboratory using MOP FV-0237.0 (EPA, 2010). Appendix C details the modifications made to the instrument and includes a complete list of all hardware components and wiring schematics used during development of the SuperMAAP.

A special LabView program (kDy Automation Solutions, Morrisville, NC, USA) was written to operate the SuperMAAP hardware and interface that hardware with the standard instrument to fulfill the functions described above. The newly developed software that controls the SuperMAAP consists of four menu bars: File I/O (input/output), Measurement, Status/Errors, and Configure (Figure 3-11). The software is easy to use, and the user is only required to input the file name and location and total aerosol and sample flows before starting the measurement. At the end of each measurement, the processed file is automatically produced and average values are calculated and displayed along with the SD and the  $R^2$  of the fitted line. Operating instructions for the instrument, including the new software, are provided in SOP 2106 (Appendix D).



**Figure 3-10. SuperMAAP configuration.**



**Figure 3-11. MAAP software – measurement view.**

Even though the SuperMAAP was built as originally designed by the expert panel assembled by EPA prior to beginning the research, it was discovered later in the program that the flow configuration shown in Figure 3-10 and associated LabView code did not isolate the instrument during filter changes as originally intended. Instead, when the head opened to allow the tape to advance, there was no sample flow and the entire sampling system was open to the laboratory atmosphere, causing the sample flow to redistribute among the remainder of the instruments connected to the tunnel. EPA conducted a detailed flow and tracer gas study to assess this problem and to determine the impact of filter changes on the other measurements. As a result of this study, a suitable correction procedure was developed for the other instruments and a correction applied to the collected data. This correction, which is further discussed in Appendix C, is applicable only to the 2- to 2.5-min period during filter changes. Steps are being taken to correct the flow path and revise the LabView code for use in future research.

### **3.3.3 LII 300**

As described earlier, the Artium Technologies LII 300 measures soot particulate concentration and primary particle size in real time. An Nd:YAG pulsed laser heats the soot particles rapidly within the measurement volume from the local ambient temperature to close to the soot

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vaporization temperature ( $> 4000$  K). Incandescence from the soot particles is detected by two detectors using appropriate line filters, and the signals are recorded for subsequent analyses. A novel method was developed for calibration of the LII (self-calibrating) based on an absolute light intensity measurement that avoids the need for calibration with a known source of soot particles. This method applies two-color pyrometry principles centered at 440 and 780 nm to determine the particle temperatures.

The instrument consists of two main units: a self-contained LII unit and a laser power supply (Figure 3-12). A water line runs between the two units to cool the laser during operation. The instrument was controlled remotely using AIMS software with the AK communication protocol modified for use in this study. The commercially available LII 300 model was slightly modified as follows for the present work:

- An external vacuum pump with rotameter was incorporated to allow control and monitoring of the air sampling flow rate to the instrument
- An independent QC check was provided to verify proper instrument operation before starting measurements. The QC check was made using an operational check lamp that tests the cleanliness of the instrument windows to determine if there is a variation higher than a specified percentage deviation in the current values compared to factory-calibrated values.

Detailed instructions for using the modified LII 300 instrument by Artium Technologies and the AIMS software are provided in SOP 2102, which can be found in Appendix E.



**Figure 3-12. Major components of the LII 300: (1) self-contained LII 300 instrument and (2) laser power supply.**

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### 3.3.4 Micro Soot Sensor (MSS)

The AVL 483 MSS is based on the photoacoustic measurement principle described previously. In the instrument measurement cell, soot (highly absorbent particles) is irradiated with modulated light from an embedded Class 4 semiconductor laser ( $808 \pm 5$  nm wavelength). Periodic heating and cooling inside the photoacoustic cell result in expansion and contraction of the carrier gas. As a result of that interaction, a sound wave is formed and detected with sensitive microphones. The signal from these microphones is subsequently analyzed electronically to determine the BC concentration down to  $1 \mu\text{g}/\text{m}^3$ . The entire sensor sensitivity (the intensity of the laser beam and the sensitivity of the microphone) is checked by means of an absorber window. The system automatically performs a check of the resonance frequency of the microphone in the measuring cell at the end of the operating state “PAUSE” indicated in the operating software.

The standard AVL MSS consists of three basic units:

- Measuring unit: AVL MSS (Figure 3-13a).
- AVL exhaust conditioning unit (Figure 3-13b).
- Pressure-reducing module with dilution cell (not shown).

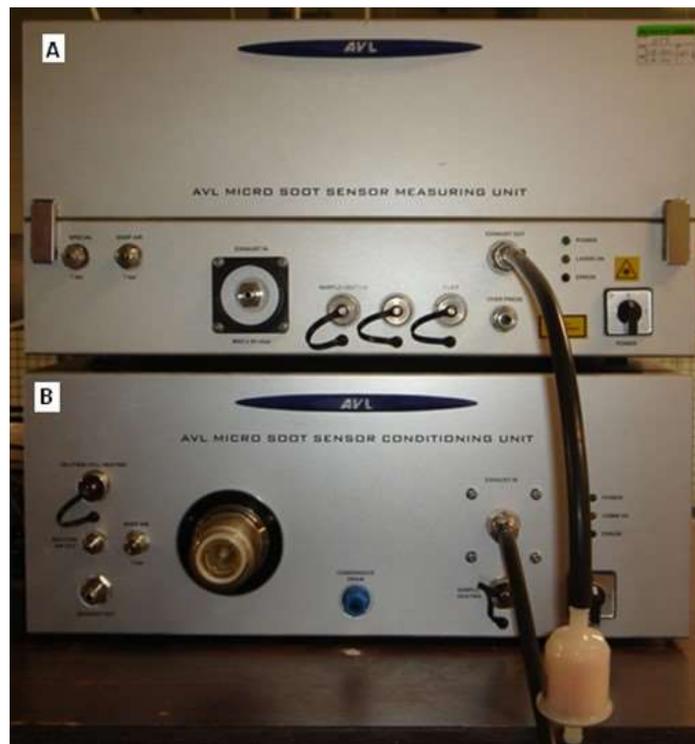


Figure 3-13. (A) AVL MSS model 483 and (B) AVL exhaust conditioning unit.

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The operating software used in this study generally restricted the input pressure of the AVL MSS measuring chamber to ambient pressure  $\pm 50$  mbar. (Note that newer versions of the software limit the input pressure to  $\pm 80$  mbar.) The temperature of the exhaust gas passing through the measuring chamber of the AVL MSS could not exceed 60 °C. To measure soot with the AVL MSS at higher exhaust gas backpressures and temperatures, the pressure and/or temperature had to be reduced. The pressure and temperature were conditioned by means of the pressure-reducing module of the AVL exhaust conditioning unit. When the ambient temperature was low and/or the exhaust gas had not been sufficiently diluted, there was a risk that condensate would form in the measuring chamber of the AVL MSS. Thus, sufficient dilution of the exhaust gas was important to prevent formation of condensate. Due to the ambient operating conditions and modest particle loading of the air stream moving through the flow tunnel, exhaust gas conditioning was not required for the current study.

The MSS was controlled with the AVL control software for conducting measurements and for displaying and storing the measurement data with a frequency up to 1 Hz. The BC mass concentrations were generated directly and expressed as concentration of soot in exhaust ( $\text{mg}/\text{m}^3$ ). The maximum soot concentration that can be measured by the MSS is  $50 \text{ mg}/\text{m}^3$  with  $1 \text{ }\mu\text{g}/\text{m}^3$  sensitivity and a published minimum detection limit of  $5 \text{ }\mu\text{g}/\text{m}^3$ .

The suction power of the pump is set with a throttling valve so that a constant sample flow of approximately 3.8 L/min is pulled into the inlet of the pump unit at a negative pressure of 300 mbar. In the measuring unit, the sample flow is split into a *bypass flow* and a *measuring flow* that passes through the measuring cell. Both flows should be approximately equal between 1.8 and 2 L/min. Thus, the AVL MSS was used as-is and without any further modifications. Detailed instructions for using the AVL MSS instrument with the conditioning unit and the control software are provided in SOP 2105, included here as Appendix F.

### 3.4 Reference Filter Sampler

Method validation was accomplished through the collection and analysis of concurrent Teflon filter samples, as specified in AIR 6037, Section 11, Technical Annex 1 (SAE, 2010). Teflon filter sampling was selected as the reference method because both the collection and analysis of the samples could be fully quality-assured using standard weights and temperature, pressure, and flow standards, all of which are NIST-traceable. The existing procedures described in Title 40 Code of Federal Regulations (CFR) Part 86.1065 were used as guidance for collection and analysis of the Teflon filter samples (EPA, 2012). Detailed instructions on collection and measurement of nvPM mass using the filter-based gravimetric method are provided in SOP 2103 (Appendix G).

A split sample was provided to the instrument(s) being evaluated and the reference filter. Measurements were then conducted over a range of soot concentrations indicative of gas turbine exhaust, and a correlation was established between the instrument readings and the gravimetrically determined PM mass concentration. Preconditioned and preweighed

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polytetrafluoroethylene (PTFE) filters were used to collect the PM mass from the main sample stream at an initial flow rate of approximately 45 L/min (Figure 3-1). However, studies have found that the QFFs used for the determination of OC/EC content described in Section 3.3.1 are also capable of adsorbing gas-phase semivolatile OC (Turpin et al., 1994) in addition to the PM OC (positive sampling artifacts). Therefore, a backup prefired QFF was installed downstream of the PTFE filter and analyzed for OC content as described in SOP 2104 (Appendix B) to correct for the total gas-phase OC measured on the primary QFF.

Finally, in the original study design, it was assumed that use of the CS would adequately remove most of the particle-phase OC from the MiniCAST exhaust so that the particles collected on the Teflon filter would have very low OC content, allowing a direct comparison of the various measurement methods with the Teflon filter values. However, the CS reduced the OC content only by an average of approximately 10 % by mass as compared to the untreated aerosol. Because of the relatively high OC content of the particles collected on the Teflon filter, some type of correction to the PM mass concentrations obtained during the gravimetric analysis was needed. Although unable to be verified experimentally, we assumed that the mass percentage of OC found on the primary QFF (after artifact correction) was identical to the mass percentage of OC found on the Teflon filter, and the total mass concentration was reduced accordingly. The OC-corrected Teflon filter concentration calculations were used during the data analyses described below.

### **3.5 Supporting Equipment**

The main supporting instruments/devices used in the study were the Model 3936 SMPS, the URG-2000-30EC PM<sub>2.5</sub> cyclone, and Personal data acquisition (PDAq) system. Each is described briefly below.

#### **3.5.1 3936 Scanning Mobility Particle Sizer**

The 3936 SMPS consists of a TSI 3080 electrostatic classifier, a TSI 3081 long differential mobility analyzer (DMA), and a TSI 3025A condensation particle counter (CPC). The SMPS was used throughout all experiments (with and without CS) to monitor PM number concentration and size distribution independently by equivalent electrical mobility diameter. The SMPS operating software was configured to cover the 13.8–723.4 nm range in the low-flow mode (3 L/min sheath air flow and 0.3 L/min aerosol flow). The impactor used a 0.0457-cm diameter orifice. Data were collected using 180-s up-scan and 15-s down-scan times. Operation of the SMPS followed MOP 1412 (EPA, 2004), which is included in this report as Appendix H.

#### **3.5.2 PM<sub>2.5</sub> Cyclone Preseparator**

An aluminum (but not Teflon-coated) PM<sub>2.5</sub> cyclone (URG-2000-30EC) designed for a flow rate of 42 L/min was used upstream of the instrumentation to capture any large particles shed from the tunnel walls (Figure 3-2). According to test data provided by the manufacturer, the cut-point

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diameter of the cyclone is  $< 1.5 \mu\text{m}$  at the approximately 90 L/min flow rate required for the suite of aerosol instruments.<sup>5</sup> The standard cyclone has a straight inlet arm and a 90-degree outlet arm equipped with special fittings. To make necessary connections with other standard Swagelok fittings and allow for leak-tight operation, the cyclone connections were refabricated in the EPA NRMRL machine shop.

### **3.5.3 Personal Data Acquisition System**

A National Instruments PDAQ/56 system was used to monitor mass flows, temperatures, and pressures throughout the flow tunnel system. The PDAQ is a 22-bit, universal serial bus (USB)–based multifunction data acquisition device that can be located up to 5 m from the personal computer (PC). The PDAQ can directly measure multiple channels of thermocouples, voltage, pulse, frequency, and digital input/output (I/O). The unit’s DasyLab software allows real-time analysis of signals from the PDAQ, conversion to operating units (L/min, mm Hg, °C, etc.), and data logging. In this study, the PDAQ recorded data for tunnel pressure and temperature, MiniCAST diluter flow, dump line flow, quartz filter sampler flow, differential pressure across the Teflon filter sampler orifice meter, and static pressure behind the Teflon sampler orifice meter (Figure 3-1).

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<sup>5</sup> A cut point of  $1.5 \mu\text{m}$  was deemed appropriate since SMPS scans of the MiniCAST exhaust showed no large particles being produced.

# 4 Experimental Procedures

## 4.1 Experimental Design

The SAE International E-31 Committee decided that each candidate method should be capable of measuring nvPM concentrations in the range 10 to 1000  $\mu\text{g}/\text{m}^3$ . Therefore, experiments were designed to encompass that concentration range. In addition, six replicate tests were conducted to provide a statistically adequate basis for comparisons.

Since the aerosol generated by aircraft gas turbine engines is a combination of both volatile and nonvolatile PM, each candidate method must be able to measure BC only without interference from volatile particles. Thus, an aerosol containing two different volatile components was evaluated using the identical experimental matrix. In the first test series, a CS was used downstream of the MiniCAST to reduce the volatile content of the test aerosol. For the second set of experiments, the CS was removed and the MiniCAST output was provided directly to the flow tunnel with no removal of the volatile component. These experiments were intended to determine the selectivity of each technique for measuring only nonvolatile soot. However, since the CS only reduced the OC content of the MiniCAST particles by approximately 10 % instead of near 100 % as expected, sensitivity of the methods to OC could not be fully assessed.

The experimental matrix used for this project is shown in Table 4-1. All four candidate methods plus Teflon filter sampling were employed at five target concentrations with six replicate tests at each concentration. In addition, the same concentrations (operating conditions) were evaluated with and without the CS to explore the influence of volatile particles.

**Table 4-1. Experimental Matrix**

Aerosol Type	Sampling Condition ID	Target Soot Concentration ( $\mu\text{g}/\text{m}^3$ )	No. of Runs	Run Time (min)
"Low" volatile PM WCS <sup>a</sup>	10WCS	10	6	420
	50WCS	50	6	360
	100WCS	100	6	180
	500WCS	500	6	40
	1000WCS	1000	6	20
"High" volatile PM WOCS <sup>b</sup>	10WOCS	10	6	420
	50WOCS	50	6	360
	100WOCS	100	6	180
	500WOCS	500	6	40
	1000WOCS	1000	6	20

<sup>a</sup> WCS = experiments with catalytic stripper = MiniCAST + CS.  
<sup>b</sup> WOCS = experiments without catalytic stripper = MiniCAST only.

The MiniCAST operating conditions (gas settings) required for the 50–1000  $\mu\text{g}/\text{m}^3$  concentration range (Table 4-2) were the same, with a fuel/air ratio of 60/1500 by volume (0.04:1). Under those conditions, soot mass concentration at the outlet of the MiniCAST measured approximately 7  $\text{mg}/\text{m}^3$  and geometric mean particle diameter was in the 80–90 nm range. To dilute the MiniCAST particle exhaust, the aerosol stream was mixed with the clean air that entered the tunnel after passing through the HEPA filters (Figure 3-1). The air was provided to the tunnel using either of two ring compressors (specifications listed in Table 3-1). The compressors are also referred to in project documentation as “big blower” and “small blower”. The big blower was employed for concentrations of 10, 50, and 100  $\mu\text{g}/\text{m}^3$  and the small blower for the 500  $\mu\text{g}/\text{m}^3$  concentration. For the highest target concentration, 1,000  $\mu\text{g}/\text{m}^3$ , a small vacuum pump capable of providing approximately 25 L/min of air was employed.

**Table 4-2. MiniCAST Flow Settings and Blower/Pump Operating Conditions**

Settings		Target Concentration ( $\mu\text{g}/\text{m}^3$ )				
		10	50	100	500	1000
MiniCAST	Propane (mL/min)	40	60	60	60	60
	Oxidation air (L/min)	1	1.5	1.5	1.5	1.5
	Nitrogen for fuel (mL/min)	200	280	280	280	280
	Quench nitrogen (L/min)	4	6	6	6	6
	Dilution air (L/min)	8	10	10	10	10
Blower/pump	Big blower	X	X	X		
	Small blower				X	
	Vacuum pump					X
	Blower/pump reading	60 Hz	40 Hz	23 Hz	10 Hz	110 on rotameter
	Tunnel flow (sLpm)	2243	1495	861	161	25

Both blowers and the vacuum pump were calibrated to find the correlation between the standard volume of air passing through the tunnel (L/min) and the blower controller readings (Hz) or the pump adjustment (rotameter reading). The results of those calibrations are shown in Appendix I with the MiniCAST settings and pump/blower conditions required to achieve the target concentrations listed in Table 4-2.

As can be seen from Table 4-2, the MiniCAST settings were different for the lowest target concentration of 10  $\mu\text{g}/\text{m}^3$ , with propane and oxidation air flow rates of 40 mL/min and 1 L/min, respectively. Although the flow rates were different and lower, the fuel/air ratio was kept constant (0.04) to produce aerosol (soot) with the same general characteristics. The other flows were also reduced proportionally.

## 4.2 Standard Operating Procedures

As discussed in Section 3, SOPs were prepared for each of the four measurement methods. Separate SOPs were also prepared for the sampling and measurement of PM mass using a

gravimetric, Teflon filter based method and for the operation of the MiniCAST. All SOPs prepared for the project are listed in Table 4-3 with the full text found in the associated appendix. EPA’s “Guidance for Preparing Standard Operating Procedures (SOPs)” (QA/G-6; EPA, 2007) was used to prepare the SOPs. Each SOP is self-contained and addresses all aspects of operation, maintenance, calibration, and QA/QC procedures suitable for possible incorporation into the ARP. Each SOP was peer reviewed by the SAE E-31 Committee’s PM Mass Measurement Team prior to beginning the measurements. The SOPs were also submitted to EPA NRMRL’s QA staff for review and approval.

In addition to the SOPs listed in Table 4-3, existing EPA MOP 1412 for operation of the TSI 3936 SMPS was also used during the validation experiments (EPA, 2004). This MOP is provided in Appendix H.

**Table 4-3. List of Developed SOPs**

SOP Number	SOP Title	Appendix
2101	Operation of MiniCAST Black Carbon Aerosol Generator from Jing Model 5201—Real Soot Generator	A
2102	Measurement of Nonvolatile Particulate Matter Mass Using the LII 300 Laser-Induced Incandescence Instrument	E
2103	Sampling and Measurement of Nonvolatile Particulate Matter Mass Using the Filter-Based Gravimetric Method	G
2104	Sampling and Measurement of Nonvolatile Particulate Matter Mass Using the Thermal/Optical Transmittance Carbon Analyzer	B
2105	Measurement of Nonvolatile Particulate Matter Mass Using the AVL 483 Micro Soot Sensor Photoacoustic Analyzer with AVL Exhaust Conditioning Unit	F
2106	Measurement of Nonvolatile Particulate Matter Mass Using the Modified Multi-angle Absorption Photometer (MAAP) – Thermo Fisher Scientific	D

### 4.3 General Operating Procedures

At the beginning of each day’s testing, several activities and procedures were performed to satisfy QA/QC requirements for each instrument and method used in the validation. These step-by-step procedures and the general protocol used to conduct each experiment were as follows:

1. Turn on all instrument computers (MAAP, LII, MSS, SMPS, and MiniCAST).
2. Using the atomic clock, set the time on the LII computer, which serves as a master clock for synchronization of all other computer clocks. The network time synchronization is automatically performed every 10 min using the ClockWatch clock card installed in the LII computer.
3. Open the main valves on the nitrogen tank and the fuel (propane) tank, and open the main compressed air valve.
4. Turn on all instruments and allow them to warm up. These instruments include AVL MSS 483 and conditioning unit; LII laser power supply (first), LII 300 instrument, and

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external vacuum pump; MAAP external pump, MAAP 5012 instrument, and SuperMAAP module; MFC system for MiniCAST; and SMPS DMA and CPC units.

5. Turn on the tunnel blower/pump and set it according to Table 4-2. The choice of blower/pump and setting will depend on target concentration.
6. Make sure the pneumatic two-way isolation valve control is in the “bypass” position.
7. Start the DasyLab software and initiate the logging.
8. Turn on the vacuum pump for the instrument excess flow (dump) line. The flow for that line is measured by an MFM and should be approximately 21 L/min. Check the DasyLab output for that line.
9. If needed, turn on the temperature controller for the CS (see Table 4-1 for details). The temperature set point should be 315 °C to reach the actual temperature of 300 °C. The CS takes approximately 10–15 min to heat up.
10. Start the AVL MSS software. Select REMOTE communication option and NO DILUTION experiment, and press the PAUSE icon. The device requires approximately 25 min to heat up. Details of instrument operation are provided in SOP 2105 (Appendix F).
11. Start the Get Red-y software for the MiniCAST MFCs. Open the main valve on the front panel of the MiniCAST, but make sure the fuel control valve is completely closed. Set the gas flows for ignition. Ignite the MiniCAST and open the fuel control valve. Inspect the sight glass to ensure the flame is still present and stable. When the flame is stable, set the gas flows per Table 4-2. Details of instrument operation are provided in SOP 2101 (Appendix A). Allow the burner to operate at least 30 min, and then start logging the MFC flows in the Get Red-y software.
12. Open the valve that supplies dilution air upstream of the CS (~ 25 L/min). The flow for that line is measured by an MFM. Check the flow for that line in the DasyLab software.
13. After the SMPS is warmed up, start the AIM software. Open and name the new file and select devices. Choose 3 L/min for the sheath air flow and 0.3 L/min for the aerosol flow, impactor type 0.0457 cm, particle density 1.000 g/cm<sup>3</sup>, and a multiple charge correction. Start data collection.
14. Place a 47-mm filter cassette containing a clean, prebaked QFF into the quartz filter holder. Install the holder in the sampler.
15. Perform a leak test for the QFF sampler. Remove the sampling line and install a pressure gauge on the inlet of the filter holder. Close the three-way valve and start the pump. Slowly open the valve and observe the pressure gauge until the maximum vacuum is reached. Close the valve and turn off the pump. Observe the pressure gauge for 2 min. If the pressure does not drop more than 15 kPa Hg, the system is leak-free.

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16. Move the three-way valve of the QFF sampler to the “bypass” (open to atmosphere) position and start the pump. When ready to sample, move the three-way valve to the “sample” position. Watch the QFF flow rate in the DasyLab software while opening the needle valve. The flow should be approximately 6 L/min.
  17. Place a 47-mm filter cassette containing a preweighed Teflon filter into the sampler filter holder and another 47-mm filter cassette containing a clean, prebaked QFF into the second filter holder. Install them in the sampler with the Teflon filter acting as the main filter and the quartz filter as a backup filter. Perform a leak test for the Teflon filter sampler using the same procedure described in step 15.
  18. Move the three-way valve of the Teflon filter sampler to the “bypass” (open to atmosphere) position and start the pump. When ready to sample, move the three-way valve to the “sample” position. Watch the Teflon filter flow rate in the DasyLab software while opening the needle valve. The flow should be approximately 45 L/min.
  19. Start the SuperMAAP software. Make sure that total and SuperMAAP flows are 5 and 3.5 L/min, respectively. Start data logging for raw data collection. Initialize a filter change. When ready, start the experiment in the software. Details on instrument operation are provided in SOP 2106 (Appendix D).
  20. Start the LII remote AIMS software. If necessary, perform a lamp check of the instrument and record the results. Start data logging. Details of instrument operation are provided in SOP 2102 (Appendix E).
  21. By this time, the AVL MSS should be warmed up. If starting a test series, perform an absorber window check. Place the AVL MSS in STANDBY position (~ 60 s for stabilizing). In SERVICE VIEW (NUMERICAL), make sure the following parameters are within the required ranges and record the results:
    - a. Zero signal (window pollution): 0.0–1.4 mV.
    - b. Resonance frequency: ~ 4100 Hz.
    - c. Maximum raw measurement value: 30–230 mV.
    - d. Measuring cell temperature at test: ~ 52 °C.
  22. Once the MSS unit has completed the STANDBY process, start sampling by selecting the MEASUREMENT option.
  23. Stop the SuperMAAP pump and perform a QC check by observing the following parameters and recording the results:
    - a. Transmission and two reflection diodes between 3000 and 3900.
    - b. Reference diode between 1500 and 3900.

When complete, turn the pump back on and force a manual filter change in the software. Details of this procedure are provided in SOP 2106 (Appendix D).

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24. After the MiniCAST has been running for approximately 30 min, check the size distribution and concentration in the flow tunnel measured by the SMPS. If the target value has been reached within approximately  $\pm 10\%$ , the system is ready to start.
  25. Start the experiment by moving the pneumatic three-way bypass valve control to the “sample” position while simultaneously pressing START CONDITION (processing data) in the SuperMAAP software. Record the START time to the nearest second. All instruments should now be measuring tunnel concentrations near the target mass concentration.
  26. During the test, record any errors, discrepancies, and other experimental observations and modifications in a laboratory notebook.

Once the test period is finished, the following steps are performed to shut down all instruments, preserve filter samples, and save the collected data:

1. End the experiment by moving the pneumatic three-way bypass valve control to the “bypass” position while simultaneously pressing STOP & CALC in the SuperMAAP software.
2. Record the STOP time to the nearest second.
3. Stop data logging in the AVL MSS software, LII AIMS software, DasyLab, SMPS AIM software, and Get Red-y software.
4. For the QFF and Teflon samplers, move the three-way valve to the “bypass” (open to atmosphere) position and stop the pumps.
5. In the Get Red-y software, set all MiniCAST gas flows to 0 to shut down the burner.
6. If done for the day, turn off the main valve on the MiniCAST and completely close the fuel control valve.
7. If done for the day, close the main valves on the propane and nitrogen gas cylinders and close the compressed air valve. Release the pressure from the propane and nitrogen gas lines.
8. If done for the day, close out the MSS, LII, DasyLab, SMPS, and Get Red-y operating software.
9. If done for the day, turn off the LII 300 instrument, laser power supply, and external pump; AVL MSS instrument and conditioning unit; SMPS DMA and CPC; MFC box for the MiniCAST; SuperMAAP instrument and external pump; and vacuum pump for dump line.
10. If done for the day, turn off the CS temperature controller (if used).
11. Leave the blower on until the next day (next test).
12. Remove the cassettes from both filter samplers (two quartz and one Teflon filter), place them in clean and labeled cassette mailers, and store them in the portable freezer until

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ready for analysis. Details about filter handling and analysis are provided in the SOP 2104 and SOP 2103 (Appendix B and Appendix G, respectively).

13. At the end of the day, copy data files to a USB memory stick and then from the stick to an office computer's hard drive.
14. Turn off all computers.

## 4.4 Data Reduction

### 4.4.1 Gravimetric Method

Total PM mass concentration was measured using 47-mm Teflon filters. The PM mass collected on a Teflon filter during sampling was determined by weighing the filter before and after sampling. The total PM mass concentration was obtained by dividing the PM mass collected on the filter by the total air volume pulled through the filter during sampling. The flow rate of sample gas through the Teflon filters was measured using an orifice meter, with the total volume of sample gas between two consecutive readings calculated by:

$$V_T = Q_{avg} t_T \quad (4-1)$$

where:

$V_T$  = total volume over the sampling time (L).

$Q_{avg}$  = average flow rate reading (sLpm).

$t_T$  = total sampling time (min).

The actual volume is the standard volume corrected to the EPA standard temperature and pressure (STP) conditions (25 °C and 760 mm Hg).

Thus, the total PM mass concentration is given by:

$$C_{PM} = M_{PM} 1000/V_T \quad (4-2)$$

where:

$C_{PM}$  = total mass concentration ( $\mu\text{g}/\text{m}^3$ ).

$M_{PM}$  = PM mass collected on the filter ( $\mu\text{g}$ ).

To correct the measured PM mass concentration from the Teflon filter results for the OC content of the QFF sample, the following calculation was used:

$$OCCC_{PM} = C_{PM} (1 - \text{Mass Fraction of OC Determined on Concurrent QFF}) \quad (4-3)$$

where:

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$OCCC_{PM}$  = organic carbon corrected total mass concentration ( $\mu\text{g}/\text{m}^3$ ).

Six experiments (runs) were conducted for each target concentration and condition. Before and after each sample set, the background air from the tunnel (MiniCAST not running) was sampled for the same sampling time as the samples from the target concentration. The mass of these “tunnel blank” filters was measured and averaged ( $OCCC_{TB}$ ) using Equations 4-1, 4-2, and 4-3. The total PM mass concentration measured using Equation 4-3 was then blank corrected ( $C_{PM-BC}$ ) as follows:

$$C_{PM-BC} = OCCC_{PM} - OCCC_{TB} \quad (4-4)$$

where:

$C_{PM-BC}$  = blank-corrected total mass concentration ( $\mu\text{g}/\text{m}^3$ ).

$OCCC_{TB}$  = average of pre- and post-test series tunnel blank concentrations ( $\mu\text{g}/\text{m}^3$ ).

#### **4.4.2 NIOSH 5040 Method**

The Sunset thermal-optical OC/EC analyzer measures the mass of EC, OC, and TC collected on QFFs in units of  $\mu\text{g}/\text{cm}^2$ . The masses (in  $\mu\text{g}$  C) of OC, EC, and TC on the filter were calculated by multiplying the concentration ( $C$ ) of each type of carbon ( $\mu\text{g}$  C/ $\text{cm}^2$ ) by the deposit area ( $A$ ) of the filter in  $\text{cm}^2$  as follows:

$$M = C A \quad (4-5)$$

The filter deposit area was  $11.76 \text{ cm}^2$  for a 47-mm quartz-fiber filter used for sampling in a filter cassette with a 38.7-mm inside diameter, which defined the deposit area. Mass ( $M$ , in  $\mu\text{g}$  C) of each type of carbon on a filter was divided by the STP volume of air sampled (Equation 4-1) to calculate concentrations (Equation 4-2) of each type of carbon sampled in the aerosol.

As already described in Section 3, a backup quartz-fiber filter was placed behind the Teflon filter to measure gas phase OC. The backup filter was analyzed using the same NIOSH 5040 method, and the concentrations of each type of carbon (OC, EC, and TC) were subtracted from the concentrations measured by the main QFF. The carbon concentrations measured by the main QFF were also blank corrected using Equation 4-4 after analyzing the “tunnel blank” filters.

#### **4.4.3 SuperMAAP**

BC mass was calculated and stored in a raw data Excel file created by the newly developed MAAP software. A processed Excel file then was automatically produced and the average concentration of BC (CBC, in  $\mu\text{g}/\text{m}^3$ ) calculated and displayed together with SD and  $R^2$  of the linear regression line. The CBC was then manually blank corrected using the average CBC measured by the MAAP in the two tunnel blank runs (see Equation 4-4). The MAAP required no additional data reduction steps.

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#### 4.4.4 LII

The LII 300 PC software (AIMS) using the AK communication protocol automatically stores data acquired during an analysis in individual Excel spreadsheet files. For the current project, BC mass concentrations were generated on a 1-Hz basis and expressed as concentration of soot in exhaust ( $\text{mg}/\text{m}^3$ ) at 25 °C and 1013 mbar (760 mm Hg). Thus, no additional STP correction was necessary. The average CBC was calculated, and that value was blank corrected with the average CBC measured by the LII in the tunnel during the two tunnel blank runs when the MiniCAST was off.

It should be noted that the LII did not produce a numerical value when the measured concentration dropped below detection. Therefore, for the tunnel blank runs, zeros were manually entered into all blank cells of the spreadsheet generated by the AIMS software, and the average concentration was calculated accordingly.

#### 4.4.5 AVL MSS

The AVL MSS PC software automatically stores data acquired during an analysis in individual Excel spreadsheet files. BC mass concentrations were generated on a 1-Hz basis and expressed as concentration of soot in exhaust ( $\text{mg}/\text{m}^3$ ) at 0 °C and 1013 mbar (760 mm Hg). The following equation was used to recalculate that value to EPA STP conditions (25 °C and 760 mm Hg):

$$C_{stp} = C \times (P/P_{stp}) \times (T_{stp}/T) \quad (4-6)$$

where:

$C_{stp}$  = soot concentration at EPA STP conditions (25 °C and 760 mm Hg).

$C$  = soot concentration at 0 °C and 760 mm Hg generated by the MSS instrument.

$P/P_{stp}$  = ratio of actual to standard pressures (in atm) under different conditions.

$T_{stp}/T$  = ratio of standard to actual temperatures (in K) under different conditions.

Since both the pressures and the temperatures are known values, the conversion can be simplified to:

$$C_{stp} = C \times 0.92 \text{ (mg/m}^3\text{)} \quad (4-7)$$

This equation accounts for the temperature conversion from 0 °C to 25 °C for the MSS.

The average CBC was also calculated, and that value was blank corrected with the CBC measured by the AVL MSS in the two tunnel blank runs (see Equation 4-4).

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## 4.5 Data Post-Processing

Upon completion of the study, QC checks of the data were performed, revealing a number of issues requiring corrective action. First, the results showed that for the soot aerosols generated by the MiniCAST, the PM mass measurements performed by the MSS and NIOSH 5040 methods were in good agreement with the OC-corrected Teflon gravimetric method. However, the LII measurements of BC mass were significantly higher (~ 138 %) and the SuperMAAP instrument measurements were lower (~ 35 %). The reasons for these variations were further investigated as discussed below. Finally, a major issue was discovered late in the program with the SuperMAAP prototype, also described below, that impacted the data collected by the other instruments. This section outlines all corrective actions taken for the LII and SuperMAAP and post-processing of the data.

### 4.5.1 LII

To diagnose problems with the LII, the instrument was returned to the manufacturer where it was discovered that the wrong calibration constant (i.e., the irradiance value from the integrating sphere was used instead of the radiance value) was applied before the instrument was shipped to EPA. Working with representatives from Artium Technologies, Inc., and NRC–Canada, the calibration was rerun and the existing LII calibration coefficients for conversion of the LII incandescence signals to BC mass were replaced with corrected values. As a result of that change, all raw LII data sets were reprocessed by Artium Technologies, Inc., and new average BC concentrations computed. However, to independently verify the new coefficients, the LII calibration change was experimentally verified as described in Appendix J. This evaluation indicated sufficient agreement between the new experimental data and the data reprocessed by Artium for the same test conditions that the reprocessed LII data could be used.

### 4.5.2 SuperMAAP

Working with Aerodyne Research, Inc., kDy Automation Solutions, Inc., and the APPCD Metrology Laboratory, the SuperMAAP and its operating software were reevaluated to determine the basis for the observed difference (~ 35 % under-measurement of BC concentration). Two problems were found that were not apparent before the study began. First, the tape head was determined to contain a leak whereby laboratory air was introduced into the flow downstream of the filter tape. Based on a recalibration of the entire flow system, it was determined that approximately 15 % less air was actually passing through the filter tape than was actually measured by the downstream MFC. Further experiments with different filter loadings showed that this leak was consistent and could easily be compensated for in the MFC calibration. In addition, the existing data set could be corrected by a simple flow correction. It is generally known that the standard 5012 MAAP is not leak tight, and this leak was thought to be minimal, which was found not to be the case.

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Another problem involved the linear regression of the MBC values used to determine the average CBC in the LabView version 1.2 software. The original code calculated the linear regression over the entire sampling period by simply ignoring the time period(s) when filter changes occurred. This method created approximately a 9 % difference in the average CBC from that determined by the Aerodyne Research IgorPro software (see Appendix C). Therefore, the LabView software code was revised to calculate individual linear regressions, statistics, and average CBC for each period between filter changes and then calculate an overall average CBC and statistics from these values. This revision provided results that were within 1 ng/m<sup>3</sup> of the value determined by the Aerodyne IgorPro code.

A LabView post-processor was developed whereby the existing experimental data could be corrected for this problem and reported accordingly. New average BC concentrations were computed using the post-processor. Independent experimental verification of the SuperMAAP changes was also deemed necessary, which showed that the post-processed results were acceptable, as discussed in Appendix J.

Finally, a major issue was discovered with the SuperMAAP prototype during use on another project, as described in Appendix C. One of the main objectives of the instrument modification was to make sure that the MAAP filter changes did not adversely affect the measurements made by other instruments operating on the same sampling line. The MAAP experts who attended the workshop held by EPA thought this problem had been solved during the design phase. However, this was found not to be the case, and a special air flow and tracer gas study (described in detail in Appendix C) was conducted to determine the impact of the SuperMAAP filter change on the other instruments and to develop appropriate correction factors. These corrections were then applied to the entire data set already corrected for the LII recalibration and the SuperMAAP leak adjustment and software change as presented in Section 5.

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## 5 Results and Discussion

The study was conducted from July 22 to October 12, 2011, and consisted of 75 test runs following the experimental matrix shown in Table 4-1. At least six runs were completed at each target concentration in addition to a tunnel blank before and after each test series. The run times varied from 7 h at the 10  $\mu\text{g}/\text{m}^3$  target concentration to 20 min at 1000  $\mu\text{g}/\text{m}^3$  to collect a consistent mass loading for the filter samples. A consistent loading was also an additional QC check during the laboratory analyses of the samples. The following sections provide the results of the study.

### 5.1 Catalytic Stripper Results

Table 5-1 shows the raw experimental data for all tests conducted with the CS. Recall that these experiments were intended to determine the selectivity of each technique for measuring soot of lower volatility. Also shown in the table are test date, start time, test duration, standard error of each value, and EC/TC ratio. These data reflect all corrections described in Section 4.5 except for the tunnel blanks (whose values are shown in the table), the SuperMAAP filter change adjustments, and correction of the Teflon data for OC content. The latter correction was found to be necessary due to the low OC removal efficiency of the CS as described previously.

Final results for each method are provided in Table 5-2. These data reflect all final corrections and are plotted against the OC-corrected Teflon filter concentrations in Figure 5-1. Figure 5-1 also shows the linear regression results (slopes and correlation coefficients) with the dashed 1:1 line representing perfect agreement between each set of measurements. Deviation from that line (i.e., slope) indicates the magnitude of experimental variability from the filter gravimetric method. The linear fit lines were forced through zero,<sup>6</sup> and their slopes indicate that the best agreement (slope = 0.97) with the filter gravimetric method was observed for the LII instrument. The values for the NIOSH 5040, MSS, and SuperMAAP were very close to each other, with the NIOSH method being lower than the Teflon filter by approximately 14 % (slope = 0.86) and the MSS instrument lower by approximately 16 % (slope = 0.84). The SuperMAAP had the least agreement of the three instruments with the Teflon filter results, with a slope of 0.82 or an 18 % deviation from the 1:1 line. The NIOSH 5040 EC concentrations should have matched very closely with those obtained from the filter gravimetric method after correction for the OC content on the quartz filters, but instead approximately a 14 % difference was found in the measurements made by the two techniques with no apparent explanation. Correlation coefficients for all regression lines were excellent with  $R^2$  values being  $> 0.99$ .

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<sup>6</sup> A linear fit through zero was based on the assumption agreed to by the SAE E-31 Committee that all instruments theoretically read zero when particles are not present in the system.

**Table 5-1. Raw Experimental Data Using Catalytic Stripper<sup>a</sup>**

Target Concentration (µg/m <sup>3</sup> ) <sup>b</sup>	Test ID	Test Date	Start Time	Duration (min)	Teflon Filter (µg/m <sup>3</sup> ) <sup>c</sup>	LII (µg/m <sup>3</sup> )	MSS (µg/m <sup>3</sup> )	SuperMAAP (µg/m <sup>3</sup> )	NIOSH 5040 EC (µg/m <sup>3</sup> ) <sup>d</sup>	EC/TC (%) <sup>e</sup>
10	A	8/23/11	09:18:00	420	17.4	10.5 ± 3.40	6.69 ± 0.560	12.8 ± 0.0864	9.95	68.4
	B	8/24/11	09:05:00	420	17.1	9.48 ± 3.04	7.03 ± 0.871	13.3 ± 0.129	10.6	70.8
	C	8/25/11	09:15:00	420	17.4	10.7 ± 3.44	7.66 ± 0.689	13.5 ± 0.124	10.7	69.6
	D	8/26/11	09:00:00	420	17.1	10.9 ± 3.56	8.04 ± 0.685	12.9 ± 0.121	8.02	63.4
	E	8/29/11	09:39:00	420	16.8	11.0 ± 3.68	8.07 ± 0.628	13.1 ± 0.115	10.9	76.2
	F	8/30/11	09:00:00	420	16.7	10.9 ± 3.64	7.62 ± 0.652	12.8 ± 0.0956	8.62	74.6
	G	8/31/11	08:30:00	420	0.325	0.0730 ± 10.4	-0.000106 ± 0.000548	0.0495 ± 0.00346	0.00	0.00
50	A	8/9/11	09:35:00	360	91.5	45.2 ± 7.05	52.3 ± 1.24	64.2 ± 0.600	55.9	68.4
	B	8/10/11	09:02:00	360	96.5	51.9 ± 7.85	55.6 ± 1.46	68.1 ± 0.627	57.2	66.7
	C	8/11/11	08:50:00	360	100	57.1 ± 8.35	56.4 ± 1.28	70.0 ± 0.604	62.6	67.9
	D	8/12/11	08:57:00	360	104	61.5 ± 8.82	60.0 ± 1.19	72.5 ± 0.652	69.7	72.6
	E	8/19/11	09:14:00	360	99.5	66.7 ± 9.69	56.0 ± 0.948	59.6 ± 0.528	64.6	70.9
	F	8/20/11	09:25:00	360	106	72.8 ± 9.91	62.5 ± 0.996	63.7 ± 0.601	67.8	67.6
	G	8/22/11	09:12:00	360	0.379	0.00465 ± 0.000198	-0.920 ± 0.000596	0.369 ± 0.126	0.00	0.00
100	A	7/22/11	12:47:00	180	4.33	8.25(10) <sup>-6</sup> ± 0.000142	-0.00140 ± 0.000608	0.0349	0.00	0.00
	B	7/25/11	09:30:00	180	173	NA	96.6 ± 4.11	115 ± 1.46	104	75.0
	C	8/1/11	14:01:00	180	171	92.4 ± 10.0	96.8 ± 1.89	120 ± 1.02	119	74.9
	D	8/2/11	09:17:00	180	167	95.6 ± 10.5	95.0 ± 1.69	114 ± 1.08	106	71.6
	E	8/2/11	13:24:00	180	164	95.1 ± 10.5	93.8 ± 0.811	115 ± 1.10	103	78.0
	F	8/3/11	09:00:00	180	159	95.7 ± 11.0	92.2 ± 1.75	110 ± 1.02	103	75.4
	G	8/3/11	12:22:00	180	159	95.0 ± 10.9	92.4 ± 2.47	115 ± 1.06	90.2	76.5
	I	8/4/11	13:03:00	180	161	97.8 ± 10.9	92.8 ± 1.18	116 ± 1.07	102	70.9
	J	8/5/11	09:02:00	180	0.740	0.00473 ± 7.91(10) <sup>-5</sup>	0.518 ± 0.565	0.0576 ± 0.230	0.00	0.00
	500	A	9/1/11	11:30:00	40	607	468 ± 32.9	370 ± 14.4	413 ± 3.34	399
B		9/1/11	12:55:00	40	599	461 ± 32.2	370 ± 14.2	417 ± 3.58	388	74.1
C		9/1/11	14:50:00	40	591	453 ± 32.4	362 ± 13.8	411 ± 3.59	390	70.9
D		9/1/11	15:50:00	40	593	454 ± 31.6	358 ± 13.6	402 ± 3.67	363	73.6
E		9/2/11	09:47:00	40	624	505 ± 35.3	383 ± 16.5	420 ± 3.80	383	74.6
F		9/2/11	10:50:00	40	618	469 ± 117	381 ± 33.3	407 ± 3.99	404	74.2
G		9/2/11	11:55:00	40	616	499 ± 35.9	380 ± 16.8	416 ± 4.00	403	74.1

Target Concentration (µg/m <sup>3</sup> ) <sup>b</sup>	Test ID	Test Date	Start Time	Duration (min)	Teflon Filter (µg/m <sup>3</sup> ) <sup>c</sup>	LII (µg/m <sup>3</sup> )	MSS (µg/m <sup>3</sup> )	SuperMAAP (µg/m <sup>3</sup> )	NIOSH 5040 EC (µg/m <sup>3</sup> ) <sup>d</sup>	EC/TC (%) <sup>e</sup>
	H	9/6/11	10:05:00	40	5.70	0.0318 ± 0.000947	0.332	0.0588 ± 0.00922	0.00	0.00
1000	A	9/9/11	08:55:00	20	1600	1130 ± 88.4	983 ± 83.4	948 ± 14.2	1000	72.9
	B	9/9/11	09:38:00	20	1630	1130 ± 91.5	998 ± 84.0	942 ± 14.1	1020	73.7
	C	9/9/11	10:15:00	20	1620	1140 ± 85.5	1000 ± 86.3	941 ± 13.9	1020	74.9
	D	9/9/11	11:00:00	20	1330	924 ± 106	818 ± 115	773 ± 14.1	799	72.1
	E	9/9/11	11:40:00	20	1310	914 ± 97.4	806 ± 118	771 ± 14.0	815	74.0
	F	9/9/11	12:30:00	20	1330	931 ± 82.9	813 ± 113	794 ± 14.5	814	72.4
	H	9/9/11	14:20:00	20	1320	914 ± 91.7	785 ± 113	760 ± 13.7	796	73.7
	I	9/9/11	15:00:00	20	15.7	1.83 ± 0.00778	1.40 ± 0.530	1.02 ± 0.332	0.00	0.00

<sup>a</sup>Experimental data after correction for LII calibration constants, SuperMAAP flow adjustment/software changes, and MSS temperature correction but without subtraction of the tunnel blanks whose values are shown in the table. All data rounded to three significant figures. The ± values shown are the sample SDs.

<sup>b</sup>MiniCAST setting #7 for all tests conducted.

<sup>c</sup>Not adjusted for the percent OC determined from the quartz filter analyses.

<sup>d</sup>EC = elemental carbon determined by the NIOSH 5040 method.

<sup>e</sup>Ratio of EC to TC determined from the quartz filter analyses.

**Table 5-2. Summary of Final Test Results Using Catalytic Stripper<sup>a</sup>**

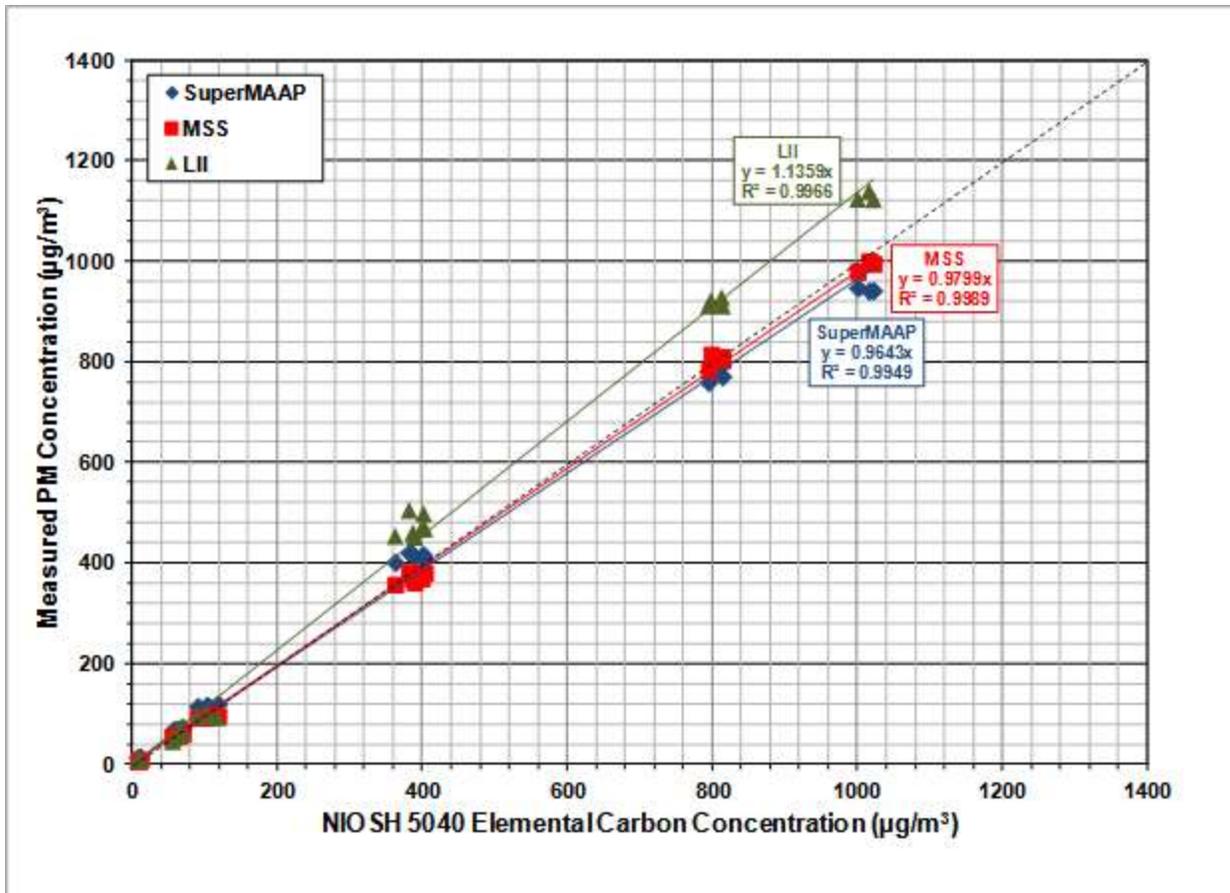
Target Concentration	Measurement Method <sup>b</sup>	OC-Corrected PM Concentration ( $\mu\text{g}/\text{m}^3$ ) <sup>c</sup>									
		Test A	Test B	Test C	Test D	Test E	Test F	Test G	Test H	Test I	Test J
10 $\mu\text{g}/\text{m}^3$	TEFLON	17.0	16.8	17.0	16.7	16.4	16.3	Blk	NA	NA	NA
	TEFLON 1	11.7	11.9	12.0	10.2	12.1	11.6	Blk	NA	NA	NA
	MAAP	12.8	13.2	13.5	12.9	13.1	12.7	Blk	NA	NA	NA
	MSS	6.69	7.03	7.64	8.04	8.07	7.62	Blk	NA	NA	NA
	LII	10.4	9.4	10.6	10.7	10.9	10.9	Blk	NA	NA	NA
	EC 1	10.0	10.6	10.7	8.02	10.8	8.62	Blk	NA	NA	NA
	OC 1	4.56	4.41	4.24	5.12	3.87	3.42	Blk	NA	NA	NA
	TC 1	14.5	15.0	15.1	13.1	14.7	12.0	Blk	NA	NA	NA
50 $\mu\text{g}/\text{m}^3$	TEFLON	90.9	96.5	99.5	104	99.5	106	Blk	NA	NA	NA
	TEFLON 1	62.2	64.3	67.6	75.3	70.6	71.7	Blk	NA	NA	NA
	MAAP	64.1	68.1	69.9	72.5	59.5	63.7	Blk	NA	NA	NA
	MSS	52.0	55.3	56.1	59.7	55.8	62.2	Blk	NA	NA	NA
	LII	45.0	51.9	57.0	61.5	66.7	72.7	Blk	NA	NA	NA
	EC 1	55.9	57.2	62.6	69.7	64.6	67.8	Blk	NA	NA	NA
	OC 1	25.9	28.6	29.5	26.4	26.4	32.5	Blk	NA	NA	NA
	TC 1	81.8	85.7	92.1	96.0	91.0	100	Blk	NA	NA	NA
100 $\mu\text{g}/\text{m}^3$	TEFLON	Blk	170	168	164	161	156	157	NA	158	Blk
	TEFLON 1	Blk	118	134	120	124	115	107	NA	118	Blk
	MAAP	Blk	114	120	114	115	110	115	NA	116	Blk
	MSS	Blk	96.2	96.4	94.7	93.4	91.9	92.1	NA	92.5	Blk
	LII	Blk	NA	92.4	95.5	95.0	95.7	95.0	NA	97.8	Blk
	EC 1	Blk	104	119	106	103	103	90.2	NA	102	Blk
	OC 1	Blk	45.9	30.0	38.2	30.7	36.1	42.0	NA	34.6	Blk
	TC 1	Blk	150	149	144	134	139	132	NA	137	Blk
500 $\mu\text{g}/\text{m}^3$	TEFLON	602	594	586	588	619	613	611	Blk	NA	NA
	TEFLON 1	453	440	416	433	462	455	453	Blk	NA	NA
	MAAP	413	416	411	401	420	407	416	Blk	NA	NA
	MSS	368	369	361	357	382	380	378	Blk	NA	NA
	LII	467	460	452	453	504	468	498	Blk	NA	NA

Target Concentration	Measurement Method <sup>b</sup>	OC-Corrected PM Concentration ( $\mu\text{g}/\text{m}^3$ ) <sup>c</sup>									
		Test A	Test B	Test C	Test D	Test E	Test F	Test G	Test H	Test I	Test J
	EC 1	399	387	390	363	382	404	402	Blk	NA	NA
	OC 1	132	136	160	130	130	140	128	Blk	NA	NA
	TC 1	530	523	549	493	512	544	542	Blk	NA	NA
1000 $\mu\text{g}/\text{m}^3$	TEFLON	1590	1610	1600	1310	1300	1320	NA	1310	Blk	NA
	TEFLON 1	1160	1190	1200	945	961	956	NA	963	Blk	NA
	MAAP	947	942	941	773	771	793	NA	759	Blk	NA
	MSS	979	995	1000	815	803	810	NA	782	Blk	NA
	LII	1120	1120	1140	921	911	928	NA	911	Blk	NA
	EC 1	1000	1020	1020	798	814	813	NA	795	Blk	NA
	OC 1	373	366	340	310	286	310	NA	284	Blk	NA
	TC 1	1370	1390	1360	1110	1100	1120	NA	1080	Blk	NA

<sup>a</sup>Final experimental data after tunnel blank correction and adjustment for Teflon filter OC content and SuperMAAP filter changes.

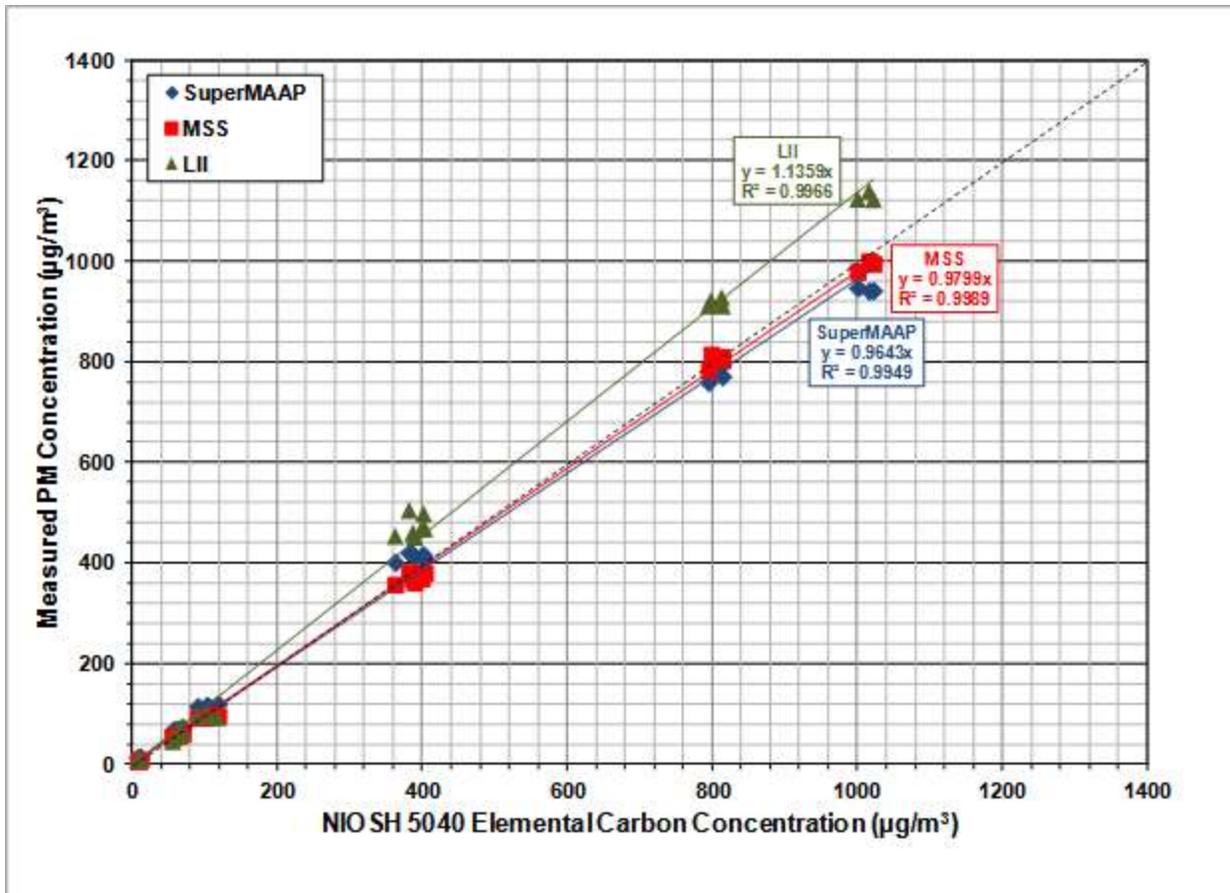
<sup>b</sup>TEFLON = Teflon filter gravimetric results with no correction for OC 1; TEFLON 1 = Teflon filter gravimetric results corrected for the percent OC determined by quartz filter sampling and NIOSH 5040 analysis; EC 1 = elemental carbon determined by NIOSH 5040; OC 1 = organic carbon determined by NIOSH 5040; TC 1 = total carbon determined by NIOSH 5040.

<sup>c</sup>All values rounded to three significant figures. Blk = blank test; NA = not applicable or not available.



**Figure 5-1. PM mass concentration plots for experiments with the catalytic stripper based on Teflon filter results.**

Similar data plotted against the NIOSH 5040 results are shown in Figure 5-2. The MSS and SuperMAAP were both within 2 to 4 % of perfect agreement; the LII was approximately 14 % higher. These results indicate that if the three instruments were calibrated against the same NIOSH standard, all three would produce comparable results. This observation is of particular importance because the NIOSH method is currently being proposed for use in routine calibration of these instruments as the filter gravimetric method is too costly and time consuming.



**Figure 5-2. PM mass concentration plots for experiments with the catalytic stripper based on NIOSH 5040 results.**

If the target concentration was limited to the 50–500  $\mu\text{g}/\text{m}^3$  range, slightly different results were obtained. This difference is illustrated in Figure 5-3A for the experimental data plotted against the OC-corrected Teflon filter results when the results for the highest (1,000  $\mu\text{g}/\text{m}^3$ ) and lowest (10  $\mu\text{g}/\text{m}^3$ ) target concentrations were eliminated from the data set. As shown in this graph, the LII slope (1.04) was within 4 % of the 1:1 line, the SuperMAAP had a 7 % slope (0.93), NIOSH 5040 had a 12 % slope (0.88), and the MSS had a 17 % slope (0.83). A slightly different outcome is observed when the instrument readings are plotted against NIOSH 5040, as shown in Figure 5-3B. Here the MSS (slope = 0.95) exhibits concentrations closest to the EC concentrations determined by the NIOSH method followed by the SuperMAAP (slope = 1.06) and the LII (slope = 1.19).

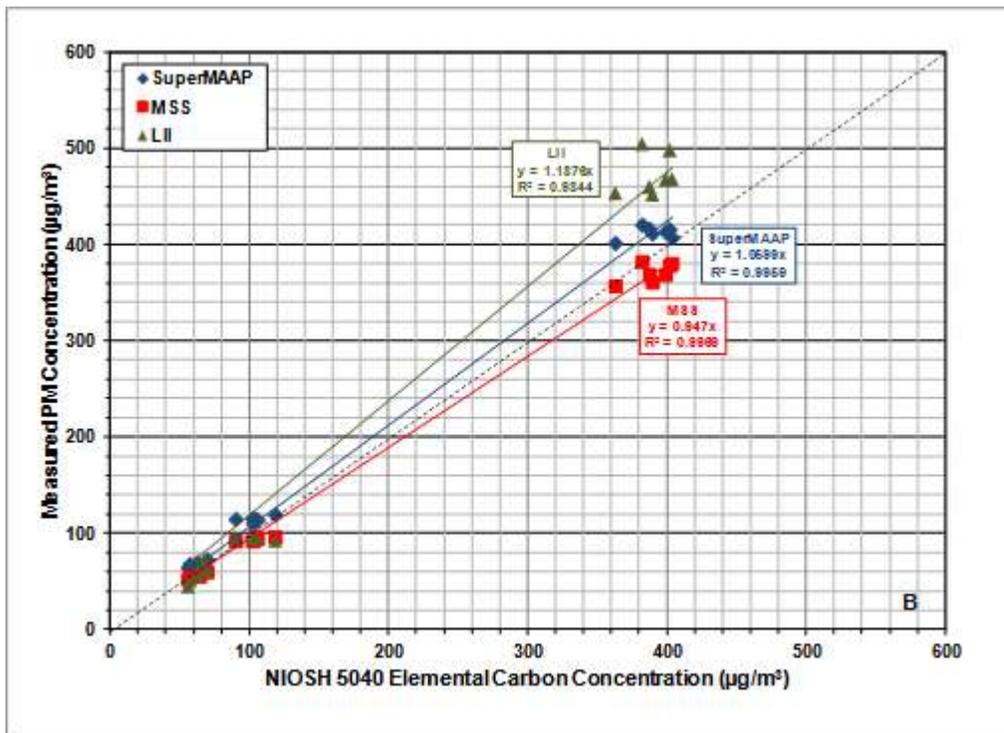
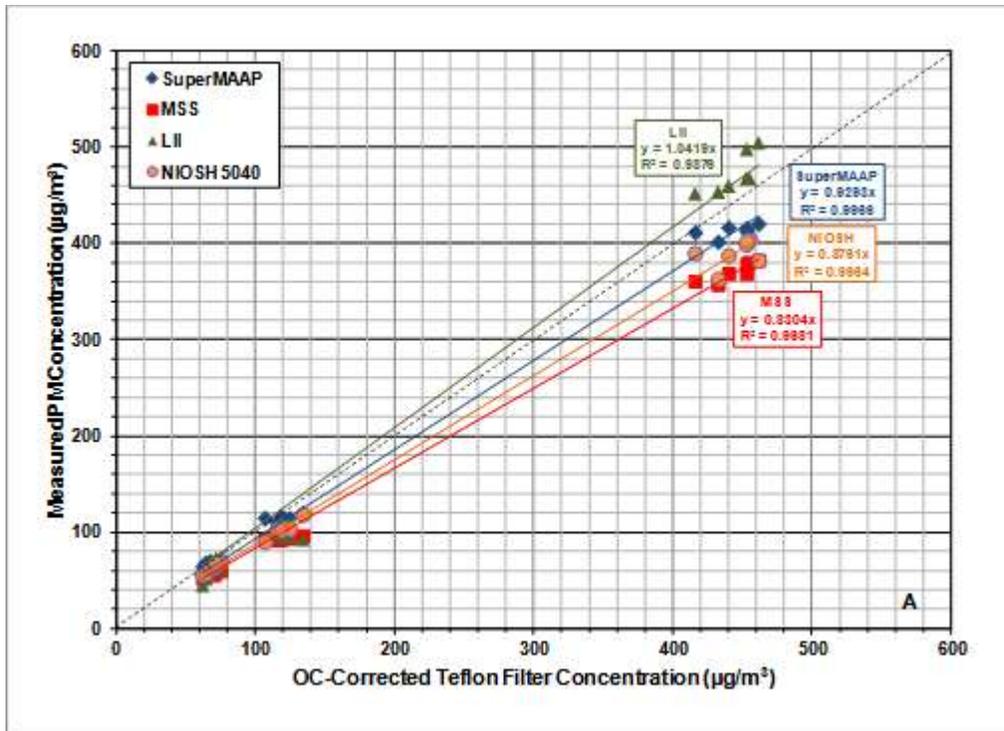


Figure 5-3. PM mass concentration plots for target concentrations between 50 and 500  $\mu\text{g}/\text{m}^3$  with stripper based on (A) OC-corrected Teflon filter results and (B) NIOSH 5040 results.

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## 5.2 Results Without Catalytic Stripper

Raw data from experiments performed without use of the CS are shown in Table 5-3. These experiments were intended to determine the selectivity of each technique for measuring soot of a higher volatile content. Again, the data shown in the table reflect all corrections except for the tunnel blank corrections, the SuperMAAP filter change adjustments, and the OC correction to the Teflon filter results, as described previously.

Table 5-4 shows the final results for each method. As before, these data reflect all final corrections and are plotted against the OC-corrected Teflon filter data in Figure 5-4. Figure 5-4 shows that, unlike the data from experiments with the CS, the NIOSH 5040 data agree within approximately 1 % of the OC-corrected Teflon filter concentrations with a slope of 0.99. The MSS results showed the next closest agreement (slope = 0.84) followed by the LII (slope = 1.19) and the SuperMAAP (slope = 0.81), both of which were within approximately 19 %. The relative relationship between the instruments is, however, generally the same as with use of the CS but with different regression slopes. All  $R^2$  values were 0.99 or greater.

Similar results were obtained when the data were plotted against the NIOSH 5040 EC concentrations, as shown in Figure 5-5. Here the MSS had the best agreement with the NIOSH method (slope = 0.85) and the LII had the worst agreement (slope = 1.21). The relative relationship of the three instruments is, however, basically the same as shown previously in Figure 5-4.

As observed for the “stripped” aerosol, a slightly different relationship between instruments was obtained if the target PM concentration range was limited to 50 to 500  $\mu\text{g}/\text{m}^3$ , as shown in Figure 5-6A and 5-6B for the data plotted against the Teflon filter and NIOSH 5040 results, respectively. The LII, NIOSH, and MSS slopes are approximately the same, as observed previously for the full range of target PM concentrations, with a significant difference shown for the SuperMAAP. The SuperMAAP agrees with the Teflon filter data within approximately 8 %, whereas before it was within approximately 19 % of the 1:1 line. A similar observation can be made for the SuperMAAP data compared with the NIOSH 5040 data shown in Figure 5-6B. Like the results with use of the stripper, the SuperMAAP seems to have better agreement with the NIOSH 5040 method for this target concentration range.

**Table 5-3. Raw Experimental Data Without Use of Catalytic Stripper<sup>a</sup>**

Target Concentration ( $\mu\text{g}/\text{m}^3$ ) <sup>b</sup>	Test ID	Test Date	Start Time	Duration (min)	Teflon Filter ( $\mu\text{g}/\text{m}^3$ ) <sup>c</sup>	LII ( $\mu\text{g}/\text{m}^3$ )	MSS ( $\mu\text{g}/\text{m}^3$ )	SuperMAAP ( $\mu\text{g}/\text{m}^3$ )	NIOSH 5040 EC ( $\mu\text{g}/\text{m}^3$ ) <sup>d</sup>	EC/TC (%) <sup>e</sup>
10	A	9/14/11	09:17:00	420	0.569	0.0336 ± 0.00101	0.763 ± 0.000649	0.108 ± 0.00691	0.00	0.00
	B	9/15/11	09:05:00	420	17.8	11.7 ± 3.85	12.1 ± 0.708	13.1 ± 0.0783	10.8	75.9
	C	9/16/11	10:55:00	420	18.9	13.0 ± 4.01	12.9 ± 0.679	14.2 ± 0.0968	12.1	82.1
	D	9/17/11	09:22:00	420	18.7	13.2 ± 4.07	13.5 ± 0.611	14.9 ± 0.104	10.5	70.7
	E	9/19/11	11:20:00	420	13.3	9.12 ± 3.44	8.34 ± 0.621	9.80 ± 0.0772	8.12	77.0
	F	9/20/11	09:00:00	420	14.8	9.44 ± 3.52	9.32 ± 0.635	10.1 ± 0.0783	8.71	72.5
	G	9/21/11	08:50:00	420	14.9	9.72 ± 3.63	8.49 ± 0.725	10.4 ± 0.0818	8.91	78.9
	H	9/22/11	08:45:00	420	0.961	0.0130 ± 0.000587	1.31 ± 0.000621	0.0369 ± 0.00115	0.00	0.00
50	A	9/23/11	12:25:00	360	97.3	51.4 ± 8.62	47.7 ± 0.661	58.4 ± 0.592	56.1	63.8
	B	9/24/11	09:30:00	360	103	58.7 ± 9.38	51.4 ± 1.00	63.8 ± 0.570	56.2	61.6
	C	9/26/11	08:53:00	360	102	59.7 ± 9.65	49.0 ± 0.916	62.1 ± 0.563	63.5	64.5
	D	9/27/11	09:00:00	360	95.2	57.5 ± 9.56	46.2 ± 0.921	59.1 ± 0.552	63.9	71.3
	E	9/28/11	09:00:00	360	100	58.5 ± 9.72	47.8 ± 1.01	59.8 ± 0.578	53.0	60.9
	F	9/29/11	10:55:00	360	100	57.1 ± 9.73	46.3 ± 0.805	58.2 ± 0.581	54.8	59.5
	G	9/30/11	10:45:00	360	0.251	0.0264 ± 0.000956	0.243 ± 0.000613	0.0553 ± 0.00230	0.00	0.00
100	A	10/2/11	09:25:00	180	179	118 ± 14.6	86.6 ± 1.33	108 ± 0.855	106	64.3
	B	10/2/11	13:10:00	180	178	114 ± 14.1	84.7 ± 0.982	110 ± 0.961	108	63.8
	C	10/3/11	09:55:00	180	177	87.4 ± 10.9	86.1 ± 1.03	107 ± 0.982	109	64.6
	D	10/3/11	13:30:00	180	176	92.2 ± 11.4	85.9 ± 1.70	100 ± 2.13	105	63.0
	E	10/4/11	10:00:00	180	188	106 ± 12.5	92.9 ± 1.08	114 ± 1.03	107	64.0
	F	10/4/11	13:20:00	180	182	104 ± 12.5	89.1 ± 1.17	113 ± 1.06	106	63.9
	G	10/5/11	09:05:00	180	0.882	0.0802 ± 0.00206	1.16 ± 0.000574	0.175 ± 0.00461	0.00	0.00
500	A	10/7/11	09:00:00	40	813	611 ± 44.6	436 ± 22.6	476 ± 4.05	528	63.5
	B	10/7/11	10:00:00	40	817	622 ± 43.1	439 ± 24.9	482 ± 4.39	507	64.3
	C	10/7/11	11:00:00	40	811	617 ± 42.0	434 ± 22.7	476 ± 4.34	495	63.5
	D	10/7/11	12:00:00	40	804	619 ± 42.8	436 ± 23.8	468 ± 4.92	535	64.9
	E	10/7/11	13:00:00	40	780	608 ± 39.4	429 ± 22.9	463 ± 4.76	527	65.9
	F	10/7/11	14:00:00	40	793	608 ± 43.5	425 ± 23.6	470 ± 4.32	491	65.0
	G	10/7/11	15:00:00	40	9.38	0.156 ± 0.00238	-0.0835 ± 0.00165	0.326 ± 0.00922	0.00	0.00
1,000	A	10/13/11	09:00:00	20	1810	1250 ± 108	893 ± 176	836 ± 19.8	1010	59.5
	B	10/13/11	09:40:00	20	1820	1310 ± 213	912 ± 204	840 ± 19.3	1050	59.9
	C	10/13/11	10:20:00	20	1830	1270 ± 220	904 ± 205	822 ± 19.3	1040	58.5
	D	10/13/11	11:00:00	20	1820	1300 ± 222	907 ± 203	836 ± 19.2	1100	61.1

Target Concentration ( $\mu\text{g}/\text{m}^3$ ) <sup>b</sup>	Test ID	Test Date	Start Time	Duration (min)	Teflon Filter ( $\mu\text{g}/\text{m}^3$ ) <sup>c</sup>	LII ( $\mu\text{g}/\text{m}^3$ )	MSS ( $\mu\text{g}/\text{m}^3$ )	SuperMAAP ( $\mu\text{g}/\text{m}^3$ )	NIOSH 5040 EC ( $\mu\text{g}/\text{m}^3$ ) <sup>d</sup>	EC/TC (%) <sup>e</sup>
	E	10/13/11	11:40:00	20	1750	1270 ± 220	883 ± 201	811 ± 19.2	1020	59.3
	F	10/13/11	12:20:00	20	1830	1300 ± 224	906 ± 196	838 ± 19.1	1110	60.9
	G	10/13/11	13:10:00	20	23.8	3.07 ± 0.00892	2.78 ± 0.00811	1.84 ± 0.444	0.00	0.00

<sup>a</sup>Experimental data after LII recalibration, SuperMAAP flow adjustments/software changes, and MSS temperature adjustment but without correction for tunnel blanks. All data rounded to three significant figures. The ± values shown are the sample SD.

<sup>b</sup>MiniCAST setting #7 for all tests conducted.

<sup>c</sup>Not adjusted for the percent OC determined from the quartz filter analyses.

<sup>d</sup>EC = elemental carbon determined by the NIOSH 5040 method.

<sup>e</sup>Ratio of EC to TC determined from the quartz filter analyses.

**Table 5-4. Summary of Final Test Results Without Use of Catalytic Stripper<sup>a</sup>**

Target Concentration	Measurement Method <sup>b</sup>	Measured PM Concentration (µg/m <sup>3</sup> ) <sup>c</sup>							
		Test A	Test B	Test C	Test D	Test E	Test F	Test G	Test H
10 µg/m <sup>3</sup>	TEFLON	Blk	17.0	18.1	17.9	12.5	14.1	14.1	Blk
	TEFLON 1	Blk	12.9	14.9	12.7	9.66	10.2	11.1	Blk
	MAAP	Blk	13.1	14.1	14.8	9.73	10.1	10.3	Blk
	MSS	Blk	11.4	12.2	12.8	7.64	8.63	7.79	Blk
	LII	Blk	11.7	13.0	13.2	9.09	9.42	9.69	Blk
	EC 1	Blk	10.8	12.1	10.5	8.13	8.71	8.91	Blk
	OC 1	Blk	3.42	2.64	4.37	2.42	3.31	2.40	Blk
	TC 1	Blk	14.2	14.7	14.9	10.5	12.0	11.3	Blk
50 µg/m <sup>3</sup>	TEFLON	96.7	102	102	94.5	99.7	99.7	Blk	NA
	TEFLON 1	61.7	62.8	65.4	67.4	60.7	59.3	Blk	NA
	MAAP	58.3	63.8	62.1	59.1	59.7	58.2	Blk	NA
	MSS	46.9	50.6	48.2	45.5	47.0	45.6	Blk	NA
	LII	51.4	58.7	59.7	57.5	58.5	57.1	Blk	NA
	EC 1	56.1	56.2	63.5	63.9	53.0	54.8	Blk	NA
	OC 1	31.9	35.1	35.0	25.7	34.0	37.4	Blk	NA
	TC 1	88.0	91.2	98.5	89.7	87.0	92.2	Blk	NA
100 µg/m <sup>3</sup>	TEFLON	178	177	177	175	187	181	Blk	NA
	TEFLON 1	115	113	114	110	120	116	Blk	NA
	MAAP	107	109	107	100	114	112	Blk	NA
	MSS	85.8	83.9	85.3	85.1	92.1	88.3	Blk	NA
	LII	118	114	87	92	106	104	Blk	NA
	EC 1	106	108	109	105	107	105	Blk	NA
	OC 1	58.6	61.0	59.9	61.9	60.1	59.6	Blk	NA
	TC 1	164	169	169	167	167	165	Blk	NA
500 µg/m <sup>3</sup>	TEFLON	805	809	803	797	773	785	Blk	NA
	TEFLON 1	511	520	510	517	509	510	Blk	NA
	MAAP	476	481	475	468	463	469	Blk	NA
	MSS	435	437	432	434	427	424	Blk	NA
	LII	609	620	615	618	607	607	Blk	NA
	EC 1	528	507	494	534	527	491	Blk	NA
	OC 1	304	283	284	290	273	264	Blk	NA
	TC 1	831	788	778	824	799	755	Blk	NA
1,000 µg/m <sup>3</sup>	TEFLON	1790	1800	1800	1790	1730	1800	Blk	NA
	TEFLON 1	1060	1080	1060	1100	1020	1100	Blk	NA
	MAAP	835	839	821	835	810	837	Blk	NA
	MSS	889	908	900	903	880	902	Blk	NA
	LII	1240	1300	1270	1290	1260	1300	Blk	NA
	EC 1	1010	1050	1040	1090	1020	1100	Blk	NA
	OC 1	689	703	738	697	699	709	Blk	NA
	TC 1	1700	1750	1780	1790	1720	1810	Blk	NA

<sup>a</sup>Final data after tunnel blank correction and adjustment for Teflon filter OC content and SuperMAAP filter changes.

<sup>b</sup>TEFLON = Teflon filter gravimetric results with no correction for OC 1; TEFLON 1 = Teflon filter gravimetric results corrected for the percent OC determined by quartz filter sampling and NIOSH 5040 analysis; EC 1 = elemental carbon determined by NIOSH 5040; OC 1 = organic carbon determined by NIOSH 5040; TC 1 = total carbon determined by NIOSH 5040.

<sup>c</sup>All values rounded to three significant figures. Blk = blank test; NA = not applicable or not available.

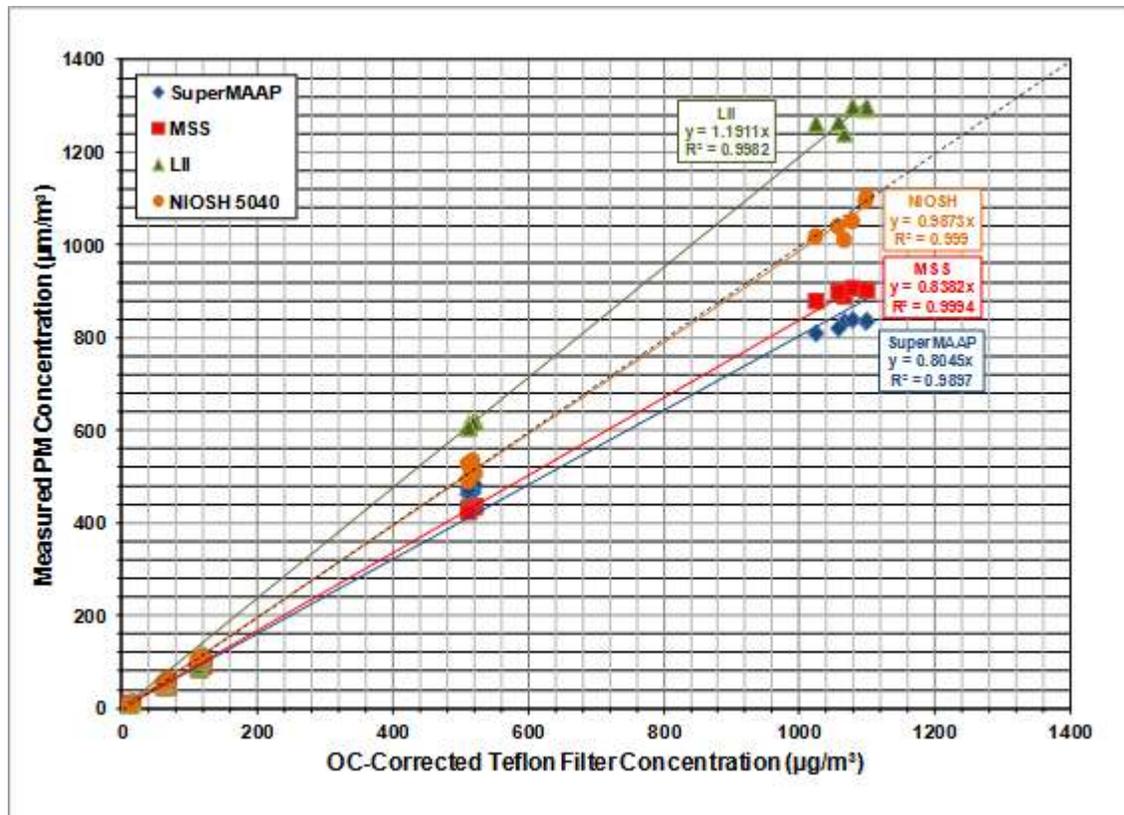


Figure 5-4. PM mass concentration plots for experiments without the catalytic stripper based on the OC-corrected Teflon filter results.

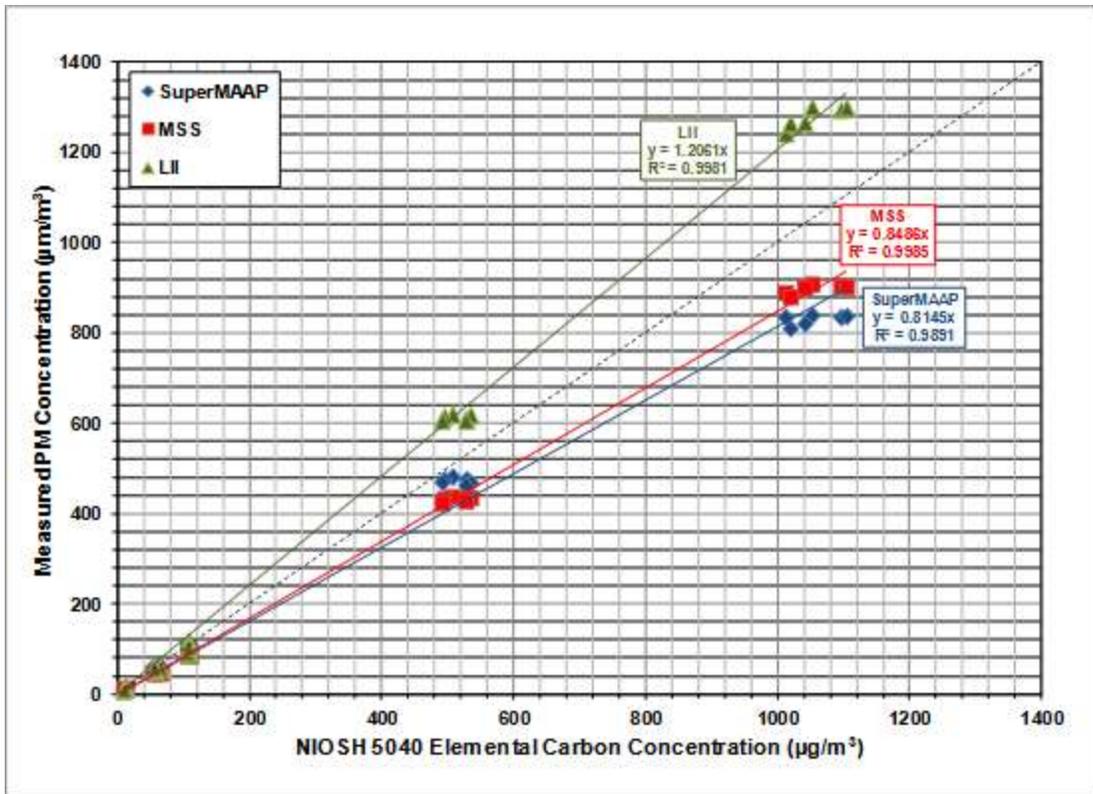


Figure 5-5. PM mass concentration plots for experiments without the catalytic stripper based on NIOSH 5040 results.

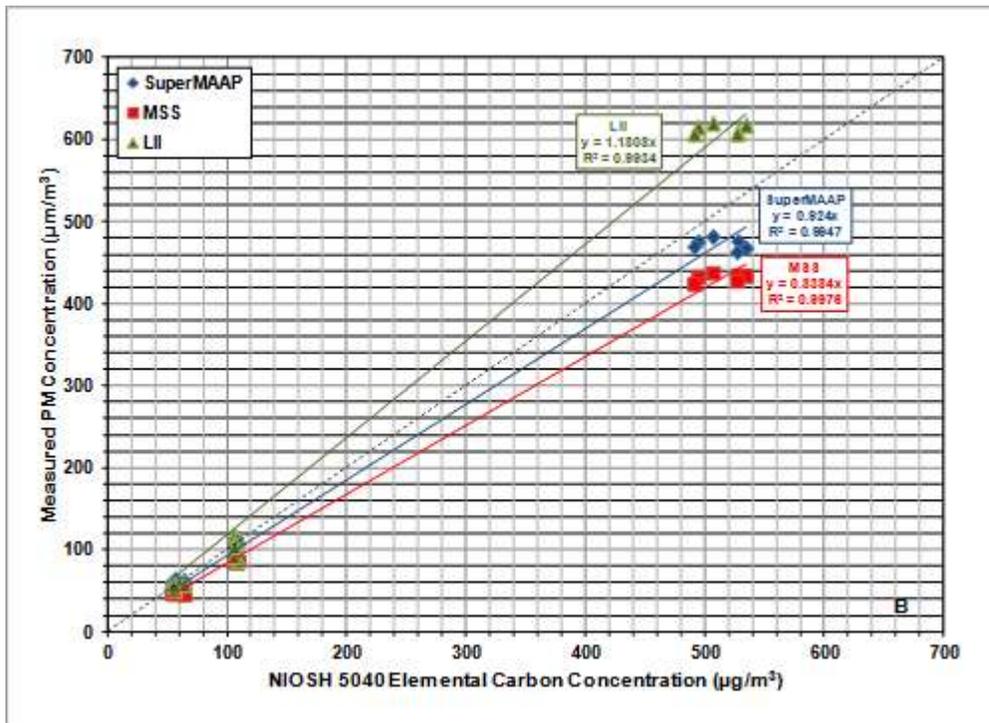
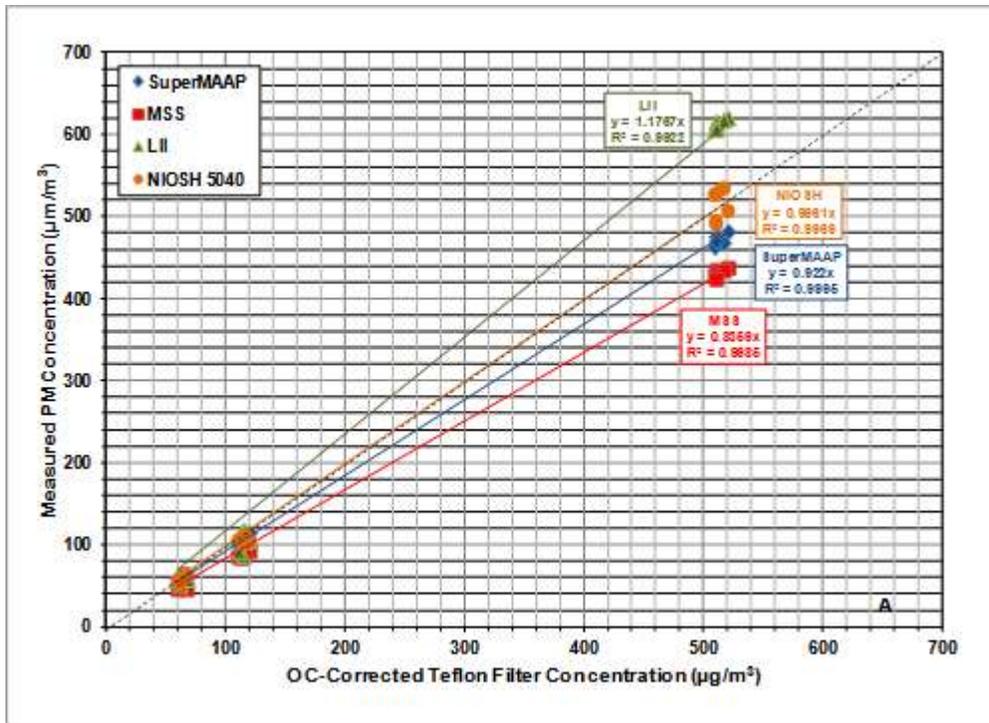


Figure 5-6. Mass concentration plots for target concentrations between 50 and 500  $\mu\text{g}/\text{m}^3$  without use of stripper based on (A) OC-corrected Teflon filter results and (B) NIOSH Method 5040.

### 5.3 Combined Experimental Results

Figure 5-7 provides the combined final results of experiments conducted with and without the CS plotted against the OC-corrected Teflon filter data. Also shown are the linear regression results and the perfect fit line. As the figure shows, both the NIOSH 5040 results and the results from the LII are within 8 % of the 1:1 line, followed by the MSS at 16 % (slope = 0.84) and SuperMAAP at 18 % (slope = 0.82). The  $R^2$  values are also  $> 0.98$ , with the MSS having the highest  $R^2$  value and the LII the lowest. The relative relationship between the four methods is also similar to the relationships presented above, with the LII generally having the highest values and the SuperMAAP the lowest compared to the Teflon filter results.

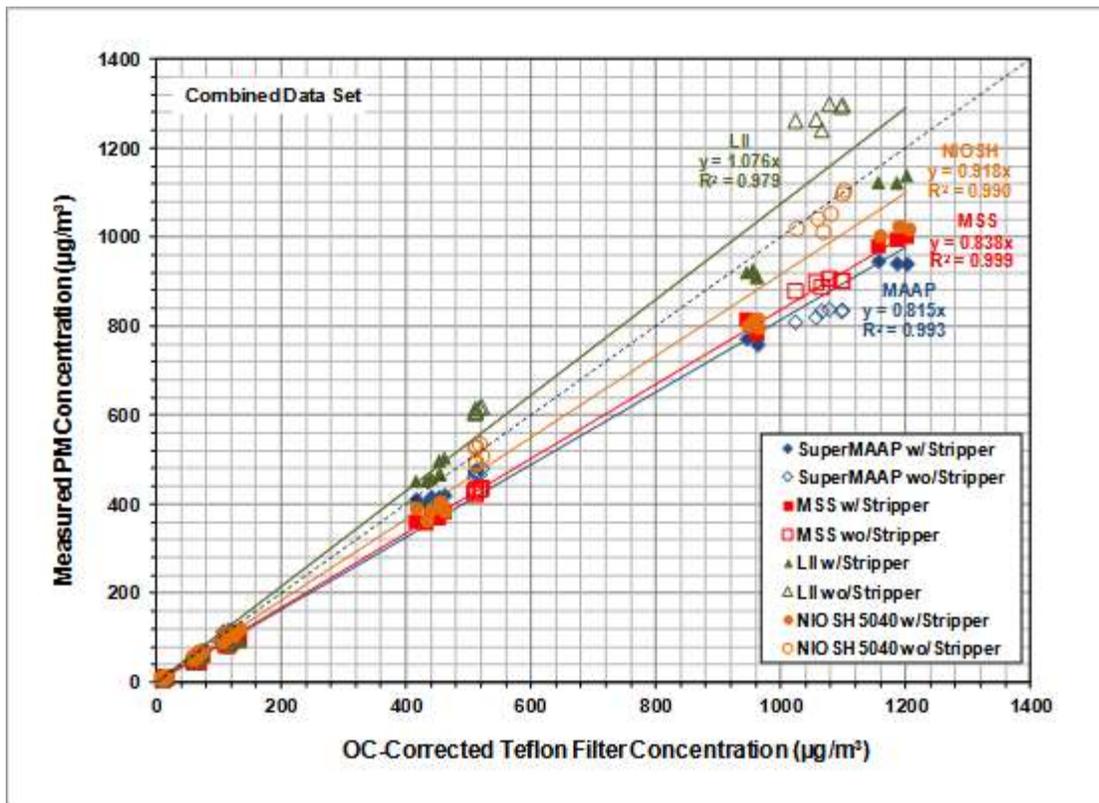
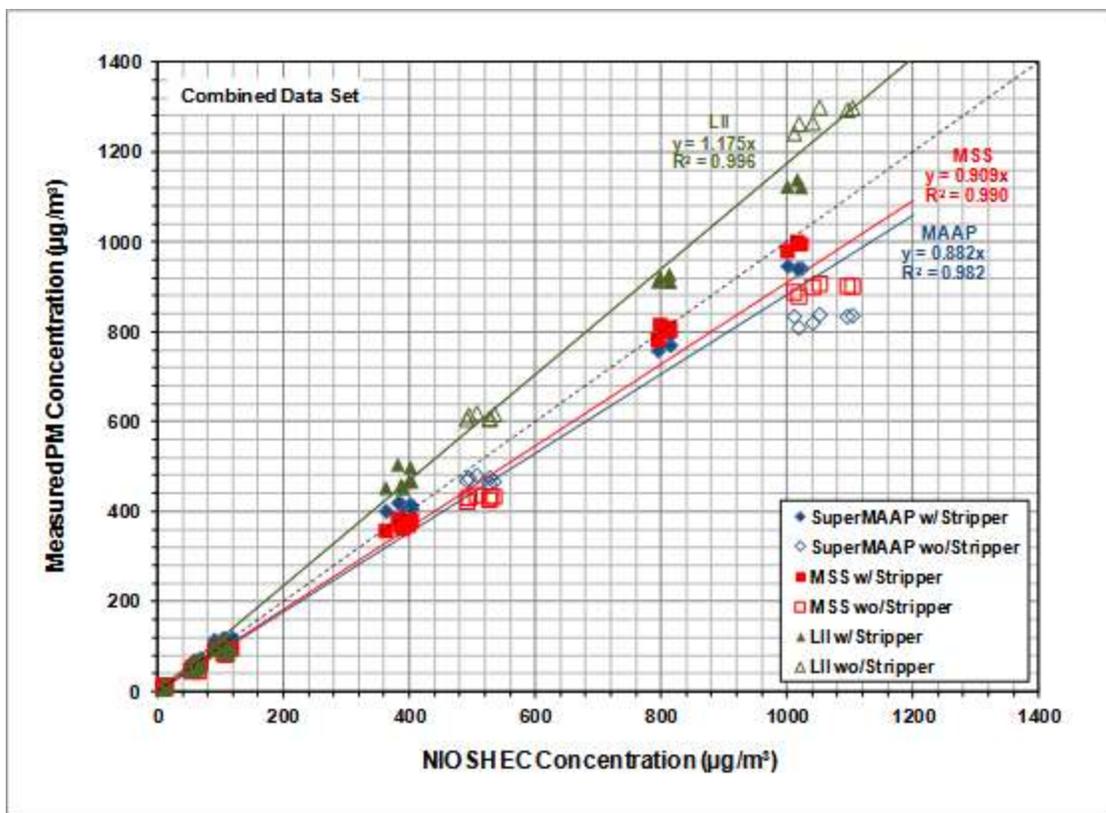


Figure 5-7. PM mass concentration plots for all experiments based on all OC-corrected Teflon filter results.

Similar results are plotted against the NIOSH 5040 EC concentrations in Figure 5-8. As shown, the best agreement was exhibited by the MSS, which was within 9 % (slope = 0.91) of the 1:1 line, followed by the SuperMAAP at 12 % (slope = 0.88) and the LII at 18 % (slope = 1.18). The relative relationship between the three instruments is, however, the same as that shown in Figure 5-7.



**Figure 5-8. PM mass concentration plots for all experiments based on all NIOSH 5040 EC results.**

Even though the correlation coefficients shown in the plots above are very good, a spread in the data with and without use of the CS can be seen for all instruments/methods. The data suggest that processing the MiniCAST aerosol through the CS changes the properties of the particles beyond the obvious reduction of OC content, which is on average only < 10 % by mass. As the particles move through the stripper, they might be increasing in density (as shown by a decrease in void space), thus influencing the optical BC measurements in the LII, MSS, and SuperMAAP. An additional investigation would be needed, however, to verify this supposition, which was beyond the scope of the current work.

Figure 5-9 shows the final experimental data with the target PM concentration range limited to 50–500  $\mu\text{g}/\text{m}^3$ . Figure 5-9A plots the data against the OC-corrected Teflon filter results and Figure 5-9B as a function of NIOSH 5040. NIOSH 5040 data compared to the Teflon filter concentrations (Figure 5-9A) exhibited a 6 % deviation (slope = 0.94) from the 1:1 line and thus the best agreement, followed by the SuperMAAP (slope = 0.93), LII (slope = 1.11), and MSS (slope = 0.833) in that order. When the LII, SuperMAAP, and MSS data are plotted against NIOSH 5040 (Figure 5-9B), the same relative relationship between instruments was observed with the SuperMAAP being within 2 % (slope = 0.98) of the perfect agreement line, followed by the MSS at 12 % (slope = 0.88) and LII at 18 % (slope = 1.18).

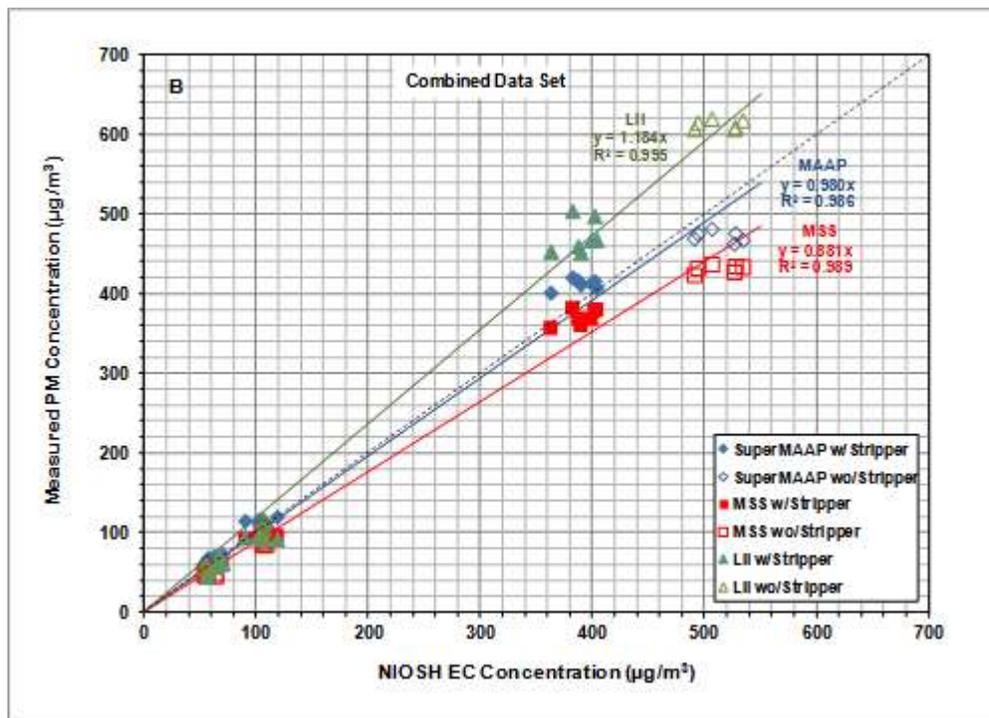
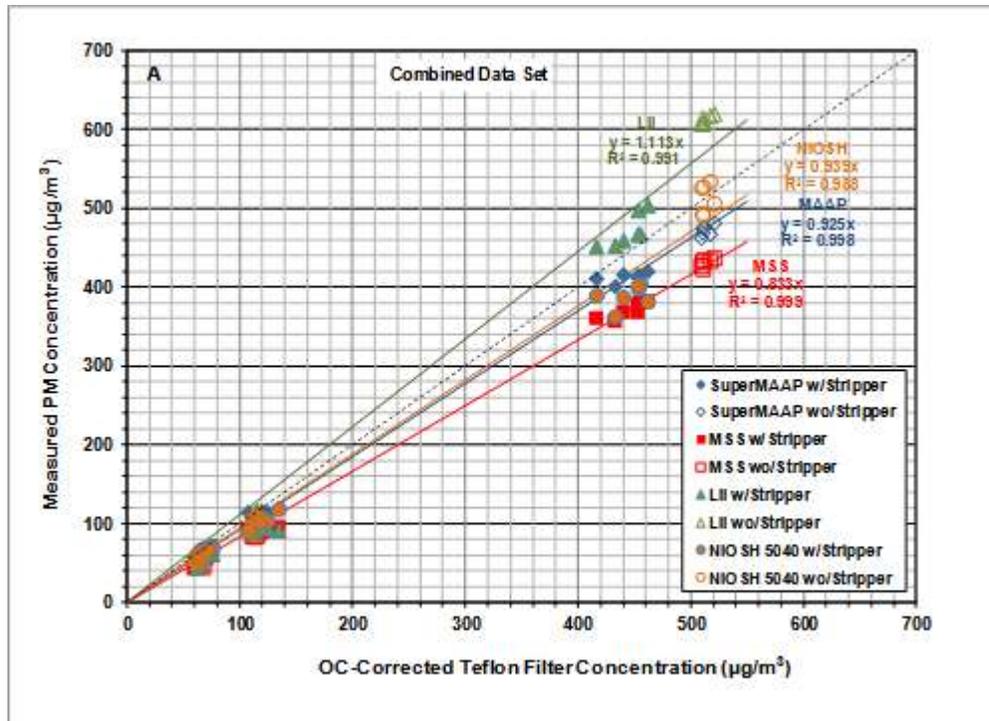


Figure 5-9. Mass concentration plots for target concentrations between 50 and 500  $\mu\text{g}/\text{m}^3$  for all experiments based on (A) OC-corrected Teflon filter results and (B) NIOSH Method 5040.

Comparing the results in Figure 5-9A to those in Figure 5-7 shows the relative position of the SuperMAAP changed from an 18 % deviation from the 1:1 line for the entire range of target

concentrations to only 7 % for target concentrations of 50–500  $\mu\text{g}/\text{m}^3$ . A much smaller change in slope was observed for the LII (from 8 % to 11 %). The data in Figure 5-9B compared to the data in Figure 5-8 show a similar result: the SuperMAAP went from a 9 % variation from the 1:1 line to only a 2 % variation. These results again suggest that the SuperMAAP and LII instruments were sensitive to the range of BC concentration measured during the experiments.

Finally, an intercomparison of the four methods was made for the combined data set. Figure 5-10 shows the LII, NIOSH, and SuperMAAP data plotted as a function of the PM concentrations measured by the MSS instrument. Also shown are the regression results and the perfect agreement line. Figure 5-10 shows the SuperMAAP (slope = 0.97) exhibited the best agreement with the MSS, followed by NIOSH 5040 (slope = 1.1) and LII (slope = 1.28). The correlation coefficients were all 0.98 or greater, indicating excellent correlation among the various techniques for all test conditions. These results further support the supposition that comparable results can be obtained by any of the methods evaluated if a common calibration source is applied to each.

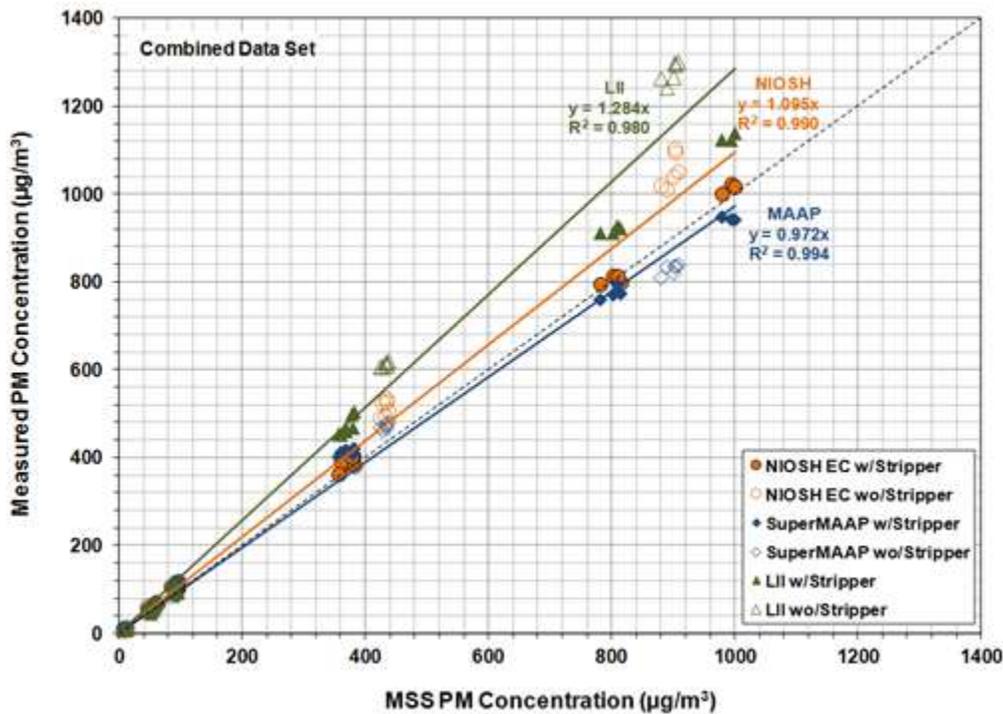


Figure 5-10. Intercomparison of measurement methods against data from the AVL MSS.

#### 5.4 General Observations

As the results above show, a high-quality data set was generated from this study. The correlation coefficients of the regression lines were typically  $> 0.98$ , which is excellent for measurements of this type. Over the entire range of target concentrations, the LII and NIOSH 5040 both had the

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highest overall agreement with the Teflon filter results, and the MSS had the best agreement with NIOSH 5040. Within the 50–500  $\mu\text{g}/\text{m}^3$  concentration range, however, NIOSH 5040 agreed best with the Teflon data and the SuperMAAP was best correlated with NIOSH 5040. In addition, both the LII and SuperMAAP showed at least some sensitivity to the PM concentration. How sensitive these instruments are to the measured PM concentration will, however, need to be evaluated using real turbine exhaust.

Given the results above, all three automated BC methods (LII, MSS, and SuperMAAP) would be expected to provide comparable results during engine certification if calibrated against a common BC source. Due to the time and expense involved, Teflon filter sampling is not a viable option for any type of routine calibration. For this reason, the SAE E-31 Committee recommended that NIOSH 5040 be used for this purpose along with a diffusion flame soot generator comparable to the one used in this study. Details of the calibration requirements have been incorporated into recently published AIR 6241 (SAE, 2013).

Finally, the SuperMAAP was developed as part of the study to explore its potential use in source measurements such as aircraft engines. Although the experimental data indicate that the SuperMAAP measurements were comparable to both the LII and MSS in this program, significant further development is needed to make it a viable alternative to the two commercially available instruments. For now, it remains strictly a research instrument until all “bugs” can be worked out.

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## 6 Quality Assurance and Quality Control

Overall data quality objectives (DQOs) established for this project were detailed in an approved QA Category III QAPP, “Validation of Non-Volatile Particulate Matter Mass Measurement Methods” (October 18, 2010). DQOs to accomplish program objectives included the following:

- Agreement of all PM mass measurement techniques with the filter gravimetric method within 5 % relative percent difference (RPD).
- Data completeness of 95 % for each test series measured as the percentage of data that satisfies the data quality indicator (DQI) goals specified in Section 6.1.
- Recovery and analysis resulting in data from at least 95 % of the total filter samples collected and/or 99 % of the continuous monitoring time scheduled.

The DQO for agreement of all techniques to be within 5 % RPD was very ambitious. When establishing DQOs, it was not known how closely these techniques would compare. This goal was not achieved for the entire data set, but agreement of techniques when compared with the reference method (Teflon filters) was generally within  $\pm 20$  % RPD with a few exceptions. The remaining DQOs were met as described.

### 6.1 Assessment of Data Quality Indicator Goals

The DQI goals that were either established originally in the QAPP or revised to reflect the criteria actually used to assess the data set are summarized in Table 6-1. Actual values calculated from the data set are also shown. Assessment of goals is discussed for each measurement in the following subsections.

#### 6.1.1 *Temperature and Pressure*

Thermocouples and pressure transducers were evaluated for precision and accuracy prior to use by the APPCD Metrology Laboratory in April 2011. Verification reports summarizing results obtained by challenging the devices with known references and the resulting estimation of uncertainty are included in Appendix K. All measurement devices were well within the established acceptance criteria, and these precision and accuracy measurements were 100 % complete.

**Table 6-1. DQI Assessment Summary**

Experimental Parameter	Measurement Method	Precision <sup>a</sup> Goal	Actual Precision	Accuracy <sup>b</sup> Goal	Actual Accuracy	% Completeness Goal/Actual
Temperature	Thermocouples <sup>c</sup>	5 °C	See 7.1.1	± 5 °C	See 7.1.1	95/100
Differential pressure	Transducers <sup>c</sup>	5 %	See 7.1.1	± 10 %	See 7.1.1	95/100
Volumetric air flow rate	MFCs and critical orifice <sup>c</sup>	5 %	See 7.1.2	± 10%	See 7.1.2	95/100
PM mass	Gravimetric analysis	3 µg	< 1.8 µg	± 15 µg	< 2 µg	95/100
OC/EC concentration	Thermo-optical analysis	10 % RSD (concentrations > 10 µg/cm <sup>2</sup> )	3.3 % RSD	90–110 % recovery	97 % recovery	95/100

<sup>a</sup>Calculated as the relative standard deviation (RSD) of the reference measurements obtained at a constant instrument set point.  
<sup>b</sup>Percent bias determined as the average variation between the reference measurements and the instrument readings over the entire operating range.  
<sup>c</sup>Includes all on-line and time-integrated instruments.

### 6.1.2 Flow Rate

The MFCs and critical orifice were verified by the APPCD Metrology Laboratory in April 2011. Verification reports summarizing results obtained by challenging the devices with known references and the resulting estimation of uncertainty are included in Appendix K. Acceptance criteria for accuracy and precision were met for all devices. These measurements were 100 % complete.

### 6.1.3 PM Mass

QA/QC of gravimetric procedures was performed as described in SOP 2103, “Sampling and Measurement of Nonvolatile Particulate Matter Mass Using the Filter-Based Gravimetric Method” (Appendix G). The types of QC samples associated with this procedure are described in Section 6.3.3. Accuracy goals were assessed by weighing 100- and 200-mg certified weights prior to each weigh session. Bias was determined as the amount of weight (in µg) the certified mass was from the mean. Precision was assessed by calculating the SD from repeated weighing of the certified weights. All acceptance criteria for accuracy and precision were met, and these measurements were 100 % complete. Results of the certified weight checks are shown in Table 6-2.

**Table 6-2. Certified Weight Verifications**

Certified Mass	Actual (Mean)	Bias	Standard Deviation
100.0000 mg	99.9985 mg (n = 19)	1.5 µg	±1.8 µg
200.0000 mg	200.0005 mg (n = 30)	0.5 µg	±1.7 µg

### 6.1.4 OC/EC Concentration

The original DQI goals established in the QAPP were not adequately stated and were changed to match the procedures described in SOP 2104, “Sampling and Measurement of Nonvolatile

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Particulate Matter Mass Using the Thermal/Optical-Transmittance Carbon Analyzer” (Appendix B). For this project, a sucrose calibration check standard was run in duplicate at the beginning of each batch of samples to assess instrument accuracy in terms of recovery and precision in terms of RSD. The accuracy acceptance criterion for the sucrose standard was 90–110 % recovery. The standard was run 66 times, with an average recovery of 97 %. The recovery range for all runs was 93–106 %, so all analyses met the established acceptance criterion. The precision goal for replicate analyses of the sucrose standard was  $\pm 10$  % RSD. The actual RSD ( $n = 66$ ) was 3.3 %, well within the DQI goal. Goals were met for all analyses for 100 % completeness.

## **6.2 Instrument Calibrations**

Calibrations of the four candidate instruments/methods and other supporting devices are described below and in the corresponding SOPs developed for those instruments and devices. Appendix K contains reports for all calibrations performed by the APPCD Metrology Laboratory.

### **6.2.1 Sunset TOT Carbon Analyzer**

As described in Section 3, the temperature calibration of the front oven thermocouple in the OC/EC TOT analyzer was performed by Sunset Laboratory and the APPCD Metrology Laboratory before the measurement campaign. The acceptance criterion was  $\pm 3$  % of the set-point temperature.

The APPCD Metrology Laboratory also performed flow sensor calibration of each of the seven needle valves on the Sunset TOT carbon analyzer before the measurement campaign. New calibration coefficients were calculated and replaced the existing coefficients in the software. A flowmeter was used periodically to confirm the calibration setting. The calibration was acceptable if the flows were within  $\pm 5$  % of actual.

In the sampling system, the MFC for the QFF sampler was calibrated by the APPCD Metrology Laboratory according to MOP FV-0237.0 (EPA, 2010) within 1 year of use.

### **6.2.2 SuperMAAP**

Two new MFCs installed in the SuperMAAP were calibrated by the APPCD Metrology Laboratory according to MOP FV-0237.0 (EPA, 2010). One MFC measured the SuperMAAP (sample) flow and the second measured the bypass flow. The APPCD Metrology Laboratory also calibrated the total aerosol flow coming into the inlet of the instrument (sample + bypass flow) and the actual sample flow drawn into the SuperMAAP detection chamber. That information was important for detecting and quantifying leaks present in the system that result from the non-leak-free design of the SuperMAAP measuring chamber. The results of these calibrations were used to generate the SuperMAAP sample and bypass slopes and intercepts implemented in the LabView software. The manufacturer performed other required calibrations of the 5012 instrument.

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### **6.2.3 AVL MSS**

The only calibration performed on the AVL MSS 483 instrument was an inlet flow check using APPCD Metrology Laboratory MOP FV-0237.0 (EPA, 2010). As stated in the instrument manual, the suction power of the pump is set with a throttling valve so that approximately 3.8 L/min are pulled at the inlet of the instrument. The flow rate was calibrated and found to be  $\pm 0.1$  % of the stated 3.8 L/min. That calibration report can be found in Appendix K. Other needed calibrations were performed by the manufacturer.

### **6.2.4 LII 300**

Flow calibration was the only calibration performed on the Artium Technology LII 300. The external pump was equipped with a rotameter that allowed control and monitoring of the air sampling flow rate to the instrument, which was calibrated by the APPCD Metrology Laboratory using MOP FV-0237.0 (EPA, 2010). The calibration report can be found in Appendix K. Other required calibrations were performed by the manufacturer.

### **6.2.5 Gravimetric Method**

Before the measurement campaign, the APPCD Metrology Laboratory calibrated the orifice flow meter for the Teflon filter sampler according to MOP FV-0201.1 (EPA, 2009a) and the two absolute pressure transducers (one in the Teflon filter sampler and one in the flow tunnel) according to MOP PR-0400.0 (EPA, 2009c). The T-type thermocouple in the tunnel flow was also calibrated by the APPCD Metrology Laboratory according to MOP TH-0301.0 (EPA, 2008) before taking measurements.

### **6.2.6 Ancillary Equipment**

Ancillary sensors and equipment were also calibrated prior to starting the measurements. The five MFCs in the PMF-42 MFC box were calibrated by the APPCD Metrology Laboratory according to MOP FV-0237.0 (EPA, 2010). The two MFMs used to regulate dilution air flow (before the CS) and excess aerosol flow (dump line) were calibrated by the APPCD Metrology Laboratory according to MOP FV-0237.0 (EPA, 2010). Finally, both blowers (big and small) and the tunnel vacuum pump rotameter were calibrated by the APPCD Metrology Laboratory to determine the correlation between the standard volume of the air passing through the tunnel (L/min) and the blower readings (Hz) and pump adjustment (rotameter reading). The results of those calibrations are in Appendix H.

## **6.3 Quality Control Procedures**

### **6.3.1 Flow Tunnel**

The flow tunnel was cleaned initially by power washing the internal surfaces using a dilute solution of laboratory detergent in deionized (DI) water, followed by a DI water rinse. After

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power washing, the tunnel was allowed to air dry. Positive pressure (~ 0.35 bar) leak checks were also performed on all sampling lines and connections with instruments and other supporting equipment to ensure leak-tight operation. Finally, tunnel blank samples for all instruments/methods were run at the beginning and end of each set of measurements for each target concentration to measure the background PM (EC/OC) concentration from the tunnel, with corrections applied to the data as described above.

### **6.3.2 NIOSH 5040**

Leak tests of the QFF sampler were performed prior to each test as described above. In addition, instrument blanks, calibration checks, and duplicate punches were analyzed for QC purposes. The instrument blank was run at the beginning of each day using a punch from a clean prefired QFF. TC values for the blank were  $\leq 0.05 \mu\text{gC}/\text{cm}^2$ . Calibration check samples (sucrose standards) were also run at the beginning of each day. The measured TC mass for the calibration standard was within  $\pm 3 \%$  of the true value. Finally, a duplicate punch for every filter sample was run. The acceptance criterion for duplicate measurements at higher filter loadings ( $\geq 5 \mu\text{g}/\text{cm}^2$ ) was based on the RPD (10–15 %) of the duplicate measurements. The acceptance criterion for duplicate measurements at low filter loadings ( $< 5 \mu\text{g}/\text{cm}^2$ ) was based on an absolute error of  $\pm 0.75 \mu\text{g}/\text{cm}^2$ . If the deposit on a filter visually appeared to be nonuniform or if a duplicate analysis was run and the duplicate measurements did not meet the appropriate acceptance criterion, the measurement was repeated.

### **6.3.3 Gravimetric Method**

Leak tests of the Teflon filter sampler were performed prior to each test as described earlier. Analytical QC was performed on the gravimetric analyses using reference filters plus reweighing of a certain percentage of the exposed filters. Reference filters were Teflon filters that remained in the weighing room in the same place and over the same preconditioning time as the sample filters. The purpose of the reference filters was to verify the cleanliness of the PM stabilization environment and to detect any unusual events that might affect PM mass on the sample filters. A reference filter met the acceptance criterion when the weight of the filter was within  $\pm 0.011 \text{ mg}$  from one weighing to the next. Also, after weighing the entire set, 20 % of the filters were subjected to reweighing. If any reweighs did not meet the previous measurement within  $\pm 4 \mu\text{g}$ , the entire set of filters was reweighed.

Gravimetric analysis results were recorded in a laboratory notebook. During this time, a total of 268 sample filters (not including reference filters) were weighed. From this batch of 268 sample filters, the records indicate that 138 filters were weighed a second time. Four reference filters were used over the time spanning the tests. Reference filters 1 and 2 were used simultaneously from the time the first gravimetric weights were recorded on March 28, 2011, through September 12, 2011. In September, a different weigh room was used for filter weighing that had two new reference filters associated with the facility. Reference filter 3 was used from September 12,

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2011, through the last record of gravimetric weights on June 25, 2012. Reference filter 4 was only used twice, once on February 15, 2012, and again on May 5, 2012.

Calibration weights (100 and 200 mg) were used to check the balance prior to each weighing session. These calibration checks were also used to assess the accuracy and precision of the gravimetric analysis.

#### **6.3.4 SuperMAAP**

QC checks of the SuperMAAP consisted of observing and recording the values of the transmission, reflection, and reference diodes on the front panel of the 5012 instrument. If any of these readings were outside of the specified range, the instrument was turned off for subsequent repair and recalibration.

#### **6.3.5 LII 300**

The operational check lamp (details provided in Appendix E) was used as an independent QC check for general operation of the instrument and to detect any system failures. The operational QC check was performed before starting each concentration set or more frequently if needed. The manufacturer had established no acceptance criterion for the lamp check. Therefore, a variation of  $\pm 10\%$  in “current” values compared to “factory” calibrated values was used as a starting point. As the study progressed, however, this criterion was determined to be too strict and values within a 20 % maximum difference between the current and factory values were used.

Other QA procedures performed on the instrument before the measurement campaign were sample cell temperature and pressure calibrations, which were performed by the manufacturer. Since the LII instrument measurements are based on absolute intensity measurements of the soot incandescence, window contamination can also systematically bias the results. Thus, the windows were examined for contamination and cleaned with a laboratory wipe before starting each test series and before performing the QC lamp check procedure described above.

#### **6.3.6 AVL MSS**

Of all the instruments, the MSS had the most highly developed QC procedures. The sensitivity of the entire sensor (the intensity of the laser beam and the sensitivity of the microphone) was checked by means of an absorber window. That QC check was carried out at the beginning of each test series. The acceptance criterion for the deviation of the measured vs. calibration value expressed as “deviation of calibration check” should be approximately 2–3 %, but not to exceed 10 %. Other QC procedures performed on the MSS included the following:

- Check of the resonance frequency of the microphone in the measuring cell performed automatically during the warmup and stabilization of the instrument.

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- Linearity check of the microphone performed before starting the measuring campaign. The resulting regression coefficient had to be higher than 0.95. Smaller regression coefficients indicated a microphone fault.
  - Linearity check of the laser performed before starting the measuring campaign. The resulting regression coefficient had to be higher than 0.95. Smaller regression coefficients indicated a laser or laser driver fault.
  - Calibration of the conditioning unit performed automatically during the warmup and stabilization of the instrument.
  - Regular maintenance:
    - Replacement of fine filters when the soot layer was visible or error 28 (flow warning) appeared.
    - Purging or replacement of sampling lines when significant pollution was visible.
    - Cleaning the measuring cell and glass tube in the measuring cell when the zero signal exceeded a value of 1.5 mV (error code 25).

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## 7 Conclusions and Recommendations

The following conclusions were reached from the study:

- The measurements made by the four BC measurement methods showed a highly linear relationship with increasing PM concentration in the flow tunnel.
- The four BC measurement techniques were found to be highly correlated with the OC-corrected Teflon reference filter values and with each other for target PM concentrations ranging from 10 to 1,000  $\mu\text{g}/\text{m}^3$ . After post-processing,  $R^2$  values were generally 0.98 or greater depending on test conditions.
- When compared with either the Teflon filter or NIOSH 5040 results, the linear regression lines of the data generated by the four techniques were within a maximum of 18 % from perfect agreement (i.e., 1:1 line) for the combined data set.
- Slightly different results were found when the range of target concentrations was limited to 50–500  $\mu\text{g}/\text{m}^3$  in the combined data set. A different relationship was also observed for the SuperMAAP and LII within this concentration range, suggesting at least some sensitivity to measured concentration.
- The high correlations observed among the various methods suggest that the LII, MSS, and SuperMAAP could provide equivalent results if calibrated against a common BC source.
- High-quality data were generated in the program with all DQI goals met or exceeded.

The following recommendations for future research are made based on the conclusions above:

- The issue of sensitivity of the three on-line instruments to volatile PM was not resolved in the current study due to the inability of the CS to significantly reduce the OC of the MiniCAST aerosol. Further research is needed to determine whether the response of these instruments will change with varying levels of OC in the PM.
- A MiniCAST burner was used in the program as a surrogate for turbine exhaust. Since major differences would be expected in the characteristics of the PM generated by a diffusion burner and an actual aircraft engine, a field evaluation is recommended to compare the four BC methods using real turbine exhaust.
- Additional research is needed to determine if the SuperMAAP and LII are sensitive to the measured concentration. Again, actual turbine exhaust should be used as the test aerosol.

In response to these recommendations, a study was conducted in September 2012 using a T-63 helicopter engine owned and operated by the U.S. Air Force Research Laboratory at Wright-

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Patterson Air Force Base in Ohio. The results of this program will be reported in a subsequent publication.

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# Appendix A: Operation of the Jing MiniCAST Model 5201 (Prototype) Black Carbon Aerosol Generator (Real Soot Generator)

STANDARD OPERATING PROCEDURE 2101

NRMRL/APPCD

APPROVED: August 18, 2011



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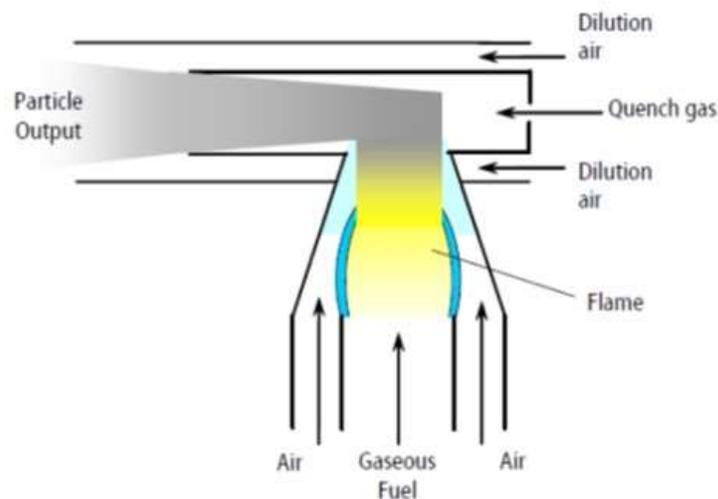
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## 1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) provides instructions for operation of the Model 5201 (prototype) MiniCAST (combustion aerosol standard) real soot generator from Jing (Bern, Switzerland). The SOP gives step-by-step procedures that describe how to install the soot generator and perform routine operations, as well as how to log the data and export them into the working files.

## 2.0 OPERATION PRINCIPLE

The MiniCAST is a soot-generating device for various applications where air containing suspended carbonaceous soot particles with adjustable and repeatable size, concentration, and chemical composition are required. As a soot source, the MiniCAST uses a propane diffusion flame, in which soot particles are formed during a pyrolysis process. In order to generate the soot particles, the oxidation air supply is kept below theoretical limits. As a consequence, particles contained within the exhaust gases arise out of the flame and leave the combustion chamber. In the next step, the particle stream is mixed with quenching gas ( $N_2$ ) in order to prevent further combustion in the particle stream and to stabilize the soot particles. This quenching inhibits condensation in the particle stream when it escapes from the flame unit to the ambient air. Subsequently, an axial flow of dilution air is supplied to reduce the concentration of the particle stream prior to exiting the MiniCAST. MiniCAST operation with different gas flows is illustrated in Figure A-1.



**Figure A-1. Operating principle of MiniCAST.**

The condition of the flame and the features of the generated soot particles, respectively, are primarily a result of the flow settings. By means of varying the flow settings, the particle size can be adjusted in a range of 20 to 200 nm (geometric mean electrical mobility diameter).

### 3.0 DEFINITIONS

**Soot:** Carbonaceous particles that are by-products of the combustion of liquid or gaseous fuels.

### 4.0 HEALTH AND SAFETY CONSIDERATIONS

- 4.1 The oxidation air and quench gas must always be present for any operation or testing purposes in order to eliminate any danger of detonation.
- 4.2 Do not release the fuel gas, by depressing the flame failure device, into the burner without oxidation air and quench gas being present.
- 4.3 Do not depress the igniter for testing purposes without the oxidation air and quench gas being present.
- 4.4 Carefully examine the connections from the fuel gas bottle to the MiniCAST to make sure they are safe and do not leak.
- 4.5 Always close the fuel gas bottle when the MiniCAST is not in use.
- 4.6 Never try to light the exhaust or unburned gases at the particle output.
- 4.7 In enclosed spaces, use a propane detector or alarm alongside the MiniCAST.
- 4.8 Always work with safety glasses to protect eyes and use heat protection gloves for manipulation of MiniCAST parts when in continuous operation.
- 4.9 Ensure that all soot escaping from the MiniCAST is removed by a ventilation system.

### 5.0 EQUIPMENT AND SUPPLIES

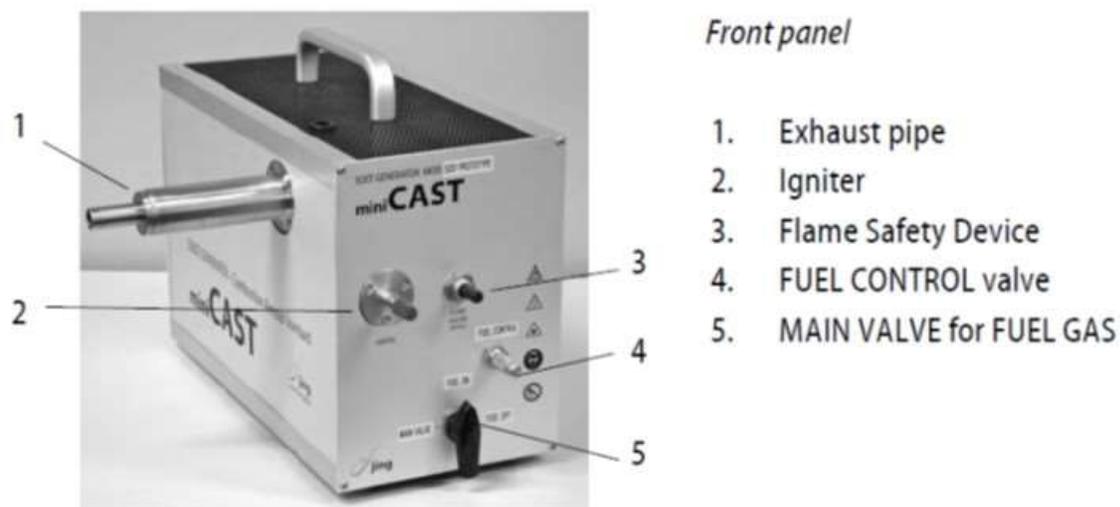
- MiniCAST soot generator from Jing.
- Propane (C<sub>3</sub>H<sub>8</sub>, purity 99.95 %) in compressed gas bottle with pressure regulator adjusted to the proper pressure required by flow controllers (0–0.150 L/min).
- Compressed air cylinder with a pressure regulator adjusted to the proper pressures required by flow controllers (0–3 L/min and 0–20 L/min).

- Nitrogen (N<sub>2</sub>, purity 99.99 %) in a compressed gas bottle or dewar with a pressure regulator adjusted to the proper pressures required by flow controllers (0–10 L/min and 0–5 L/min).
- Five mass flow controllers (MFCs), either ordered separately or mass flow control box (Model PMF-42) from Jing, with installed controllers inside.

## 6.0 PROCEDURES

### 6.1 Instrument Setup

1. Connect the input connectors of MFCs for OXIDATION AIR, QUENCH GAS N<sub>2</sub>, DILUTION AIR, and MIXING GAS N<sub>2</sub> via regulators to the corresponding gas bottle or gas supply facilities.
2. Connect the input connector of the FUEL gas MFC via a regulator to the fuel gas bottle (use flame protection valve).
3. Connect the output connectors of the MFCs for OXIDATION AIR, QUENCH GAS N<sub>2</sub>, DILUTION AIR, MIXING GAS N<sub>2</sub>, and FUEL to the corresponding connectors on the rear panel of the MiniCAST.
4. Make sure there are no leaks, especially for the fuel gas.
5. Completely close (clockwise) the FUEL CONTROL valve (4 in Figure A-2).
6. Connect the MiniCAST to the power supply.
7. Open the main valves of each gas bottle or gas supply facilities to be used.
8. Adjust the regulators of the gas bottles to the corresponding gas pressure valves shown in Table A-1.
9. Disconnect all particle analyzers from the exhaust outlet or set the exhaust outlet to ambient conditions.



**Figure A-2. Front panel of MiniCAST.**

**Table A-1. Flow and Input Pressure Ranges of MFCs for Device Settings**

Gas	C <sub>3</sub> H <sub>8</sub>	Mixing gas (N <sub>2</sub> for fuel)	Oxidation air	Quench gas (N <sub>2</sub> )	Dilution air
Flow rate (l/min)	0.04-0.08	0-0.50	0.5-2.0	6	10
Input pressure P1 of MFC	3 bar ~ 30 psig	3 bar ~ 30 psig	3 bar ~ 30 psig	2 bar ~ 15 psig	2 bar ~ 15 psig

## 6.2 Instrument Startup

1. Start computer with Red-y software for MFC manipulation.
2. Set the flow rates of each gas flow to the values shown in Table A-2.

**Table A-2. Flow Conditions for Starting MiniCAST**

$C_3H_8$	Mixing gas $N_2$ for fuel	Oxidation air	Quench gas	Dilution air
l/min	l/min	l/min	l/min	l/min
0.06	0	1.50	3	10

3. Turn on the MAIN VALVE (5 in Figure A-2).
4. Depress (open) and hold the flame safety device (3 in Figure A-2) for 4–5 seconds and then release (close) it.
5. After 5–10 s, depress the igniter (red button, 2 in Figure A-2) to ignite the pilot flame. At the same time, check through the sight glass that a weak blue pilot flame appears and stays on.
6. After a blue flame appears, immediately depress the flame safety device (3 in Figure A-2) and keep the button fully depressed. While doing that, the small blue flame should become larger.
7. While still keeping the flame safety device fully depressed, slowly turn on (counterclockwise) the FUEL CONTROL valve (4 in Figure A-2).
8. Release the flame failure device and make sure through the sight glass that the flame is present and stable.
9. Make sure that the soot is coming out of the exhaust outlet and the surplus soot can be removed by the ventilation system.
10. Change the quench gas flow to 6.5 L/min and wait for 5 min.
11. Select the operation point (Table A-3) and wait 10–15 min of stabilization time before starting the particle measurements.
12. Do the following if the flame lighting is not successful:
  - a. Fully close (clockwise) the FUEL CONTROL valve (4 in Figure A-2), set the flow for propane to 0 L/min, and close the main valve of the propane gas bottle.
  - b. Make sure that the installation and the pressure from the gas bottle are correct.
  - c. Make sure that the flow of oxidation air is present.
  - d. Make sure that there are no fuel leaks.
  - e. Open the main valve of propane gas and repeat steps 2 through 8.

An illustrative scheme for the steps required to ignite the flame on the MiniCAST is shown in Attachment 1.

**Table A-3. MiniCAST Operating Points**

OP	Results		Gas settings				
	Particle size	PM	C <sub>3</sub> H <sub>8</sub>	Oxi. air	Mix. Gas N <sub>2</sub> for fuel	Quench gas N <sub>2</sub>	Dilution air
	[nm]	[mg/m <sup>3</sup> ]	[ml/min]	[l/min]	[ml/min]	[l/min]	[l/min]
1	25.2		60	1.0	350	6.0	10
2	37.1		60	1.1	350	6.0	10
3	46.3		60	1.2	350	6.0	10
4	80.7	11.6	60	1.2	250	6.0	10
5	97.5		60	1.2	200	6.0	10
6	68.0		60	1.5	300	6.0	10
7	86.4	7.3	60	1.5	280	6.0	10
8	90.1		60	1.5	275	6.0	10
9	107.2		60	1.5	250	6.0	10

### 6.3 Stop the Operation

1. Turn off the MAIN VALVE (5 in Figure A-2).
2. Set the flow rate of the MFC for fuel gas to zero.
3. Set the flow rates of the MFCs for all other gases used during operation to zero.
4. Disconnect the MiniCAST from the power supply.
5. Close the main valves of each gas bottle or gas supply facilities.
6. Completely close (clockwise) the FUEL CONTROL valve (4 in Figure A-2).

### 6.4 Data Logging and Export

1. In the Red-y software, choose the data logger function (Figure A-3).
2. Each device (MFCs) must be selected in the list in order for its data to be collected (loggers selected are marked with an asterisk in Column “L”).
3. Select “data points” to be collected, for example, flow (default), set point, and temperature.

4. Select “kind of logging,” for example, “endless” for time unlimited runs.
5. For each device, the minimum data collection interval (“timer”) is raised by 500 milliseconds. Thus, in the case of five devices, the minimum interval is 2.5 seconds.
6. Select “directory” where the files will be logged.
7. When ready to start logging, press “Logging; to stop logging press “Stop.”

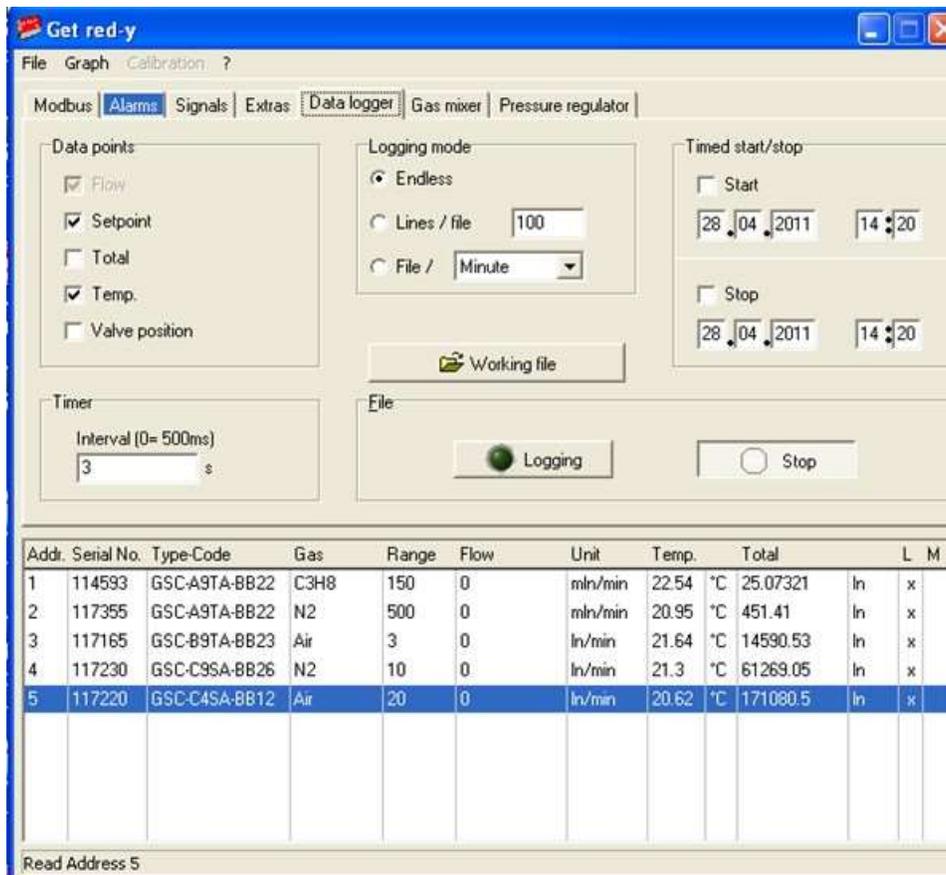
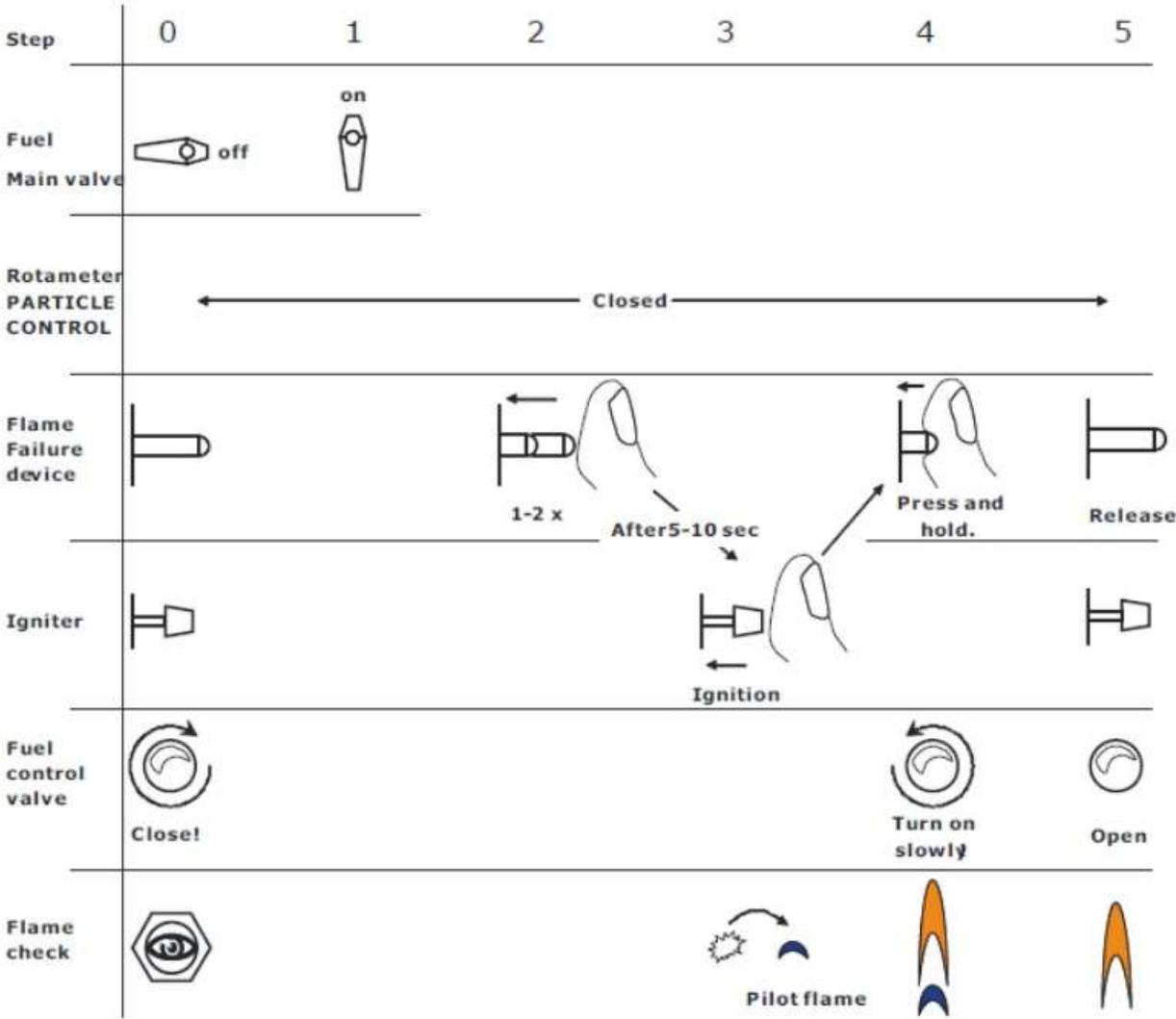


Figure A-3. Data logger – online view.

7.0 ATTACHMENTS

Illustrative Scheme for Ignition Steps



# Appendix B: Sampling and Measurement of Nonvolatile Particulate Matter Mass Using the Thermal/Optical Transmittance Carbon Analyzer

STANDARD OPERATING PROCEDURE 2104

NRMRL/APPCD

APPROVED: August 18, 2011



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## 1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) provides instructions for collection and measurement of nonvolatile particulate matter (PM) mass using the Sunset Laboratory Inc. (Tigard, OR, USA) thermal/optical–transmittance (TOT) carbon analyzer. The analytical procedure of the SOP is in accordance with the existing National Institute for Occupational Safety and Health (NIOSH) Method 5040 for diesel PM analysis.

This method includes determination of organic carbon (OC), elemental carbon (EC), and total carbon (TC) in PM collected on quartz-fiber filters (QFFs). The PM emitted from aircraft engines is composed primarily of nonvolatile particles that form inside the engine combustor, and this method can be used to quantify the emissions of nonvolatile PM (mostly EC) at the exit plane of aircraft gas turbine engines. It also addresses the formation of OC as an artifact due to conditioning and transport of the sample. The Sunset analyzer reports the OC and EC contents in  $\mu\text{g}/\text{cm}^2$  of filter area. The instrument has a detection limit on the order of  $0.2 \mu\text{g}/\text{cm}^2$  filter area for both OC and EC.

This SOP is a step-by-step procedure that describes how to perform the sampling and run the instrument as well as collect the data and perform calibrations and calculations.

## 2.0 METHOD SUMMARY

The TOT method is used to speciate carbon in PM collected on QFFs into OC and EC. In the first (non-oxidizing) heating stage, OC is thermally desorbed from the filter under a flow of helium with controlled temperature ramps. The oven is then partially cooled, and the original flow of helium is switched to an oxidizing carrier gas ( $\text{He}/\text{O}_2$ ). In the second (oxidizing) heating stage, the original EC plus pyrolyzed OC formed during the first heating stage are oxidized/desorbed from the filter with another series of controlled temperature ramps. All carbon evolved from the sample is converted to  $\text{CO}_2$  in an oxidizing oven immediately downstream from the desorption oven, and the  $\text{CO}_2$  is converted to methane ( $\text{CH}_4$ ) by a methanator oven before being measured with a flame ionization detector (FID).

## 3.0 DEFINITIONS

**Organic carbon (OC):** Optically transparent carbon at  $\sim 670 \text{ nm}$  removed (through the thermal desorption or pyrolysis) and char deposited when heating a filter sample to a preset maximum ( $850 \text{ }^\circ\text{C}$ ) in a non-oxidizing ( $\text{He}$ ) carrier gas.

**Elemental carbon (EC):** Carbon that can only be removed from the filter under an oxidizing carrier gas ( $\text{He}/\text{O}_2$ ). Optically absorbing carbon removed at high temperatures in a non-oxidizing carrier gas when internal (sample matrix) oxidants are present.

## 4.0 INTERFERENCES

**Pyrolytically produced elemental carbon (PyC):** Laser transmittance is used to optically correct for pyrolytically produced EC (or char or PyC) formed from organic compounds during the first (non-oxidizing) part of the analysis. Formation of PyC decreases the transmittance of the laser beam through the filter. During the oxidizing part of the analysis, all EC (including PyC) is burned off the filter. The split between OC and EC is assigned by the calculation software as the time during the analysis when the transmittance of the laser beam rises back to its initial value at the beginning of the analysis. Total FID response to the left of the split is assigned to OC, and total FID response to the right of the split (but before the internal standard peak) is assigned to EC. PyC is defined as carbon evolved between the addition of oxygen and the OC-EC split. If the OC-EC split occurs before the addition of oxygen, PyC is zero. An example thermogram for a filter sample is shown in Attachment 11.1.

The NIOSH 5040 method for diesel PM analysis has fixed residence times at each temperature step within the He and He/O<sub>2</sub> phases and a maximum temperature for the He phase of 870 °C. The NIOSH 5040 temperature profile used in the present study is documented in Attachment 11.2. Some studies (Chow et al., 2001) argue that 870 °C is too high and promotes more charring, thus resulting in the OC-EC split shifted to the right side of the thermogram and higher measured OC concentrations (lower EC) compared to some other low-temperature protocols (Interagency Monitoring of Protected Visual Environments [IMPROVE] protocol).

The split between OC and EC can be inaccurate if the sample transmittance is too low. The EC loading at which this occurs depends on the laser intensity. In general, the OC-EC split can be inaccurate when EC loadings are above 20 µg/cm<sup>2</sup>.

## 5.0 HEALTH AND SAFETY CONSIDERATIONS

- 5.1 Before attempting any repairs, turn off power and wait for all heated zones to cool.
- 5.2 Do not look directly at the laser source as permanent eye damage can occur.
- 5.3 Handle all support gas cylinders and regulators with caution. Always have cylinders properly chained to a safety rack.
- 5.4 Handle the quartz boat with extreme caution, and regularly clean and maintain the boat to ensure that it is free of all deposits.
- 5.5 Inspect the punch regularly for any unevenness around the sharp edges. Punches with one or more significant notches in the sharp edges should be replaced. Clean

the punch between samples by rubbing the cutting edges with a piece of clean quartz filter.

## 6.0 EQUIPMENT AND SUPPLIES

### 6.1 Instrumentation

- Sunset Laboratory dual-optics carbon analyzer, including the following:
  - Computer system that meets Sunset Laboratory's specifications for running the analyzer, storing the analysis data, and performing calculations.
  - Color printer (for printing thermograms).
  - Sunset Laboratory instrument operation software version 230 (OCECInst230x.exe) or newer.
  - Sunset Laboratory calculation software version 151 (OCECCalc151.exe).
- Vacuum pump capable of providing 6 L/min.

### 6.2 Ancillary Equipment

#### 6.2.1 Sampling

- 47-mm stainless steel filter holder meeting Title 40 Code of Federal Regulations Part 1065, Subpart B, requirements.
- 47-mm prebaked quartz filters (Tissuequartz™ 2500 QAT-UP from Pall Corporation, catalog #7202 or equivalent) with associated polytetrafluoroethylene (PTFE) cassettes meeting Title 40 Code of Federal Regulations Part 1065, Subpart B, requirements.
- Electronic mass flow controller (MFC; Dwyer Model GFC-1133 or equivalent) with 9.53-mm (3/8-in.) outside diameter (OD) inlet/outlet fittings calibrated by the APPCD Metrology Laboratory according to MOP FV-0237.0 within 1 year of use; MFC readings are recorded by a computerized data acquisition system (DAS) running the DasyLab® software package. Approximately 1 meter of stainless steel or Teflon sampling line to interconnect the above components downstream of the filter holder.
- Brass or stainless steel three-way switching valve with 9.53-mm (3/8-in.) OD fittings.

- Brass or stainless steel needle valve with 9.53-mm (3/8-in.) OD inlet/outlet fittings.
- Sterile Petri dishes (Pall Corporation, catalog #7242 or equivalent).
- Aluminum foil.
- Laboratory timer with 1-s resolution.
- Cassette separator – anodized aluminum (Airmetrics, USA catalog # 600-007 or equivalent).
- Cassette mailers – antistatic (Airmetrics, USA catalog # 600-008 or equivalent).
- Computerized DAS with DasyLab<sup>®</sup> software package.
- Vacuum pump suitable of providing ~6 L/min.

#### **6.2.1 Analysis**

- Precision punches (nominal area 1.0 cm<sup>2</sup> and 1.5 cm<sup>2</sup>).
- Syringes or automatic pipettors (10 µL calibrated).
- Forceps with rubber tips (for manipulation of quartz boat).
- Tweezers (for manipulation of quartz filter samples and punches).
- Clean QFFs.
- Analytical balance (capable of weighing to ±0.0001 g) recertified by the APPCD Metrology Laboratory within 1 year of use.
- Class 1 weights.

#### **6.3 Reagents**

- Helium, ultra-high purity (UHP).
- Hydrogen, UHP, or hydrogen generator.
- Oxygen (10%) in helium, premixed, purified.
- Methane (5%) in helium, premixed, certified.
- Air, ultra-zero.
- Sucrose, 99.9% reagent grade.
- Organic-free water.

### **7.0 PROCEDURES**

## 7.1 Quartz-Fiber Filter Preparation

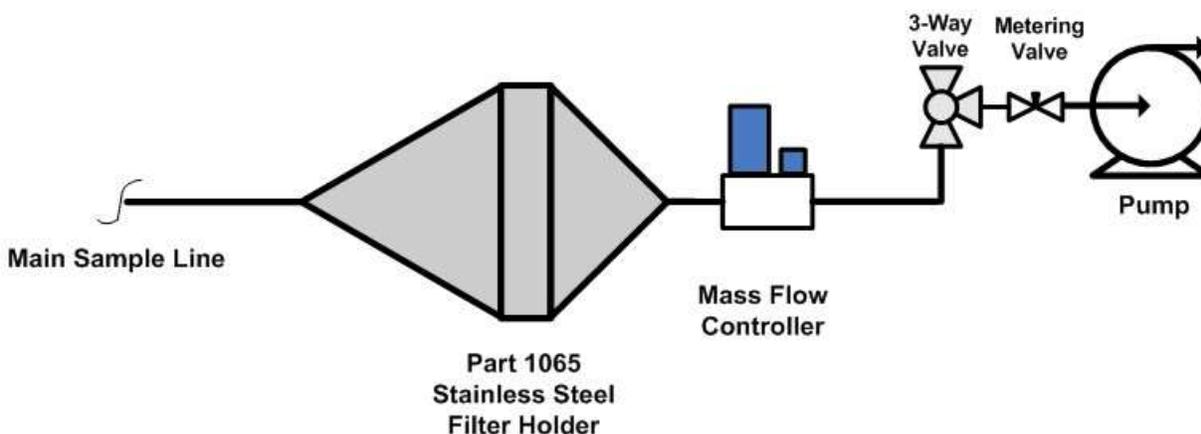
New QFFs usually have an OC background of 2 to 5  $\mu\text{g}/\text{cm}^2$ , which must be removed prior to analysis. To eliminate this background, purchased QFFs must be:

- Prebaked in a muffle furnace at 550 °C for 12 hours before sampling.
- Stored in Petri dishes lined with clean aluminum foil (also baked at 550 °C for 12 hours). After baking, aluminum foil is rinsed in n-hexane and dried in the oven at 100 °C for 10 min. Aluminum foil liners must be cut to cover the inside surfaces of the Petri dishes so that the filters do not directly touch the dish when placed inside the lined dishes.

The filters and liners must be handled with Teflon forceps to avoid any contamination.

## 7.2 Sampling Procedure

1. Assemble the QFF sampling train as illustrated in Figure B-1 and connect equipment to the stainless steel sampling line provided by others.



**Figure B-1. Quartz filter sampling train.**

2. Install a 47-mm filter cassette containing a prebaked QFF into the filter holder per the manufacturer's recommendations.
3. Conduct a leak check of the system by removing the sampling line and installing a vacuum gauge on the inlet of the filter holder. Start the pump with the three-way valve in the "bypass" (open to atmosphere) position. Before proceeding, close the metering valve and then just crack the valve to restrict

the rate at which the vacuum is placed on the system to avoid tearing the filter. Make sure that power is applied to the MFC before proceeding. Switch the three-way valve to the “sample” (straight through) position, observe the vacuum gauge until the maximum vacuum is reached, and then switch the three-way valve back to the “bypass” position. Observe the vacuum gauge for a period of 2 min. If the vacuum drops more than 127 mm (5 in.) Hg, the system has a leak. Turn off the pump and slowly release the vacuum by switching the three-way valve to the “sample” position. Once the vacuum has been released, remove the vacuum gauge from the sampling train inlet. If a leak is found, locate and repair the leak and repeat the above procedure.

4. To prepare for sample collection, move the three-way valve to the “bypass” (open to atmosphere) position and start the pump. When sampling conditions become stable, switch the three-way valve to the “sample” (straight through) position and record the start time to the nearest second.
5. Sample for a sufficient period to accumulate at least  $0.2 \mu\text{g}/\text{cm}^2$  of sample mass (for more accurate results at least  $2 \mu\text{g}/\text{cm}^2$ ) on the QFF per NIOSH Method 5040. At the end of this period, move the three-way valve back to “bypass,” stop the timer, and record the end time to the nearest second.
6. Stop the pump and remove the filter cassette from the filter holder. Place it in a clean and labeled cassette mailer. If another run is to be made, install a fresh filter cassette in the filter holder and repeat Steps 3 through 6.
7. Remove the filter from the cassette using the cassette separator and place it in an aluminum foil-lined Petri dish. Samples should be stored in a freezer at  $\sim -20 \text{ }^\circ\text{C}$  until ready for analysis.
8. Collect at least one field blank for every 10 filter samples collected. A field blank shall consist of installing and immediately removing a QFF cassette in the filter holder without actually passing any air through the filter.

### 7.3 Standards Preparation and Analysis

A set of external liquid calibration standards containing sucrose in organic-free water is used to establish the linearity of the FID response and to calibrate the gaseous internal standard (5% methane in helium) that is injected at the end of each analysis.

During TOT analysis of sucrose, some OC (the only kind of carbon in sucrose) is volatilized and some OC is pyrolyzed during all four of the non-oxidizing heat ramps. As a result, all OC fractions and PyC show up in the thermogram.

#### 7.3.1 Preparation of Standards

**Sucrose Stock Solution:** A sucrose stock solution is prepared by weighing  $10.000 \pm 0.010$  g sucrose into a 1000 mL volumetric flask and diluting to the mark with organic-free water. (10.000 g of sucrose [ $C_{12}H_{22}O_{11}$ , MW = 342.31] in 1,000.00 mL of solution has a carbon [C, AW = 12.01] concentration of  $4.210 \mu\text{gC}/\mu\text{L}$ ).

$$\frac{10.000 \text{ g sucrose}}{1000.00 \text{ ml solu}} \times \frac{12 \times 12.01 \text{ g C}}{342.31 \text{ g sucrose}} \times \frac{1 \text{ ml}}{10^3 \mu\text{l}} \times \frac{10^6 \mu\text{g}}{1 \text{ g}} = 4.210 \frac{\mu\text{g C}}{\mu\text{l solu}}$$

**Calibration Standards:** At least three calibration standards that span the measurement range of the samples are prepared. Calibration standards are prepared either (1) by weighing appropriate masses of sucrose into a volumetric flask and diluting to the mark with organic-free water, or (2) by diluting aliquots of the sucrose stock solution (section 1a) with organic-free water in a volumetric flask. A typical set of calibration standards includes the sucrose stock solution (nominally  $4.2 \mu\text{gC}/\mu\text{L}$ ) and two dilutions of the sucrose stock solution (to  $2.1 \mu\text{gC}/\mu\text{L}$  and  $0.42 \mu\text{gC}/\mu\text{L}$ ). Normally,  $10.0 \mu\text{L}$  of each standard is used in a calibration analysis, but a larger volume of the sucrose stock solution could be used to extend the measurement range.

Sucrose stock solution and sucrose calibration standards are stored in a refrigerator at  $\leq 4 \text{ }^\circ\text{C}$ . New stock solution and calibration standards are prepared at least every 6 months.

### 7.3.2 *Calibration with External Standards*

External standards are used to establish linearity of FID response and to calibrate the 5 % methane in helium internal standard loop. Prepare and spike filter punches with external standards for calibration and analyze them according to the following instructions:

1. A new, clean section of a quartz filter is punched out (1 cm<sup>2</sup> punch area) and the section is placed on the quartz filter boat in the analysis oven.

(The filter punch section remaining in the oven from the last analysis can be used instead of a new section of filter).

2. An “Oven Clean” cycle is run to completely clean the filter section; then an “Instrument Blank” is run.
3. The quartz door to the oven is opened and the quartz filter boat containing the cleaned filter punch is taken out.
4. Using a precision syringe, a 10.0- $\mu$ L volume of a standard sucrose solution is delivered to the clean filter punch without removing the punch from the filter boat.

(Deposit the standard at the location on the punch that will be directly in the path of the laser during analysis).

5. The filter boat is put back into the oven, the quartz door of the oven is closed, and the filter is allowed to dry completely (10–20 min) inside the cool oven before the start analysis button is clicked.
6. The filter punch is analyzed as described in next Section 7.4.
7. Sections 3 through 6 are repeated until all three standards have been analyzed and all of the following criteria have been met:
  - The three-point calibration has an  $R^2 \geq 0.998$  (linear least-squares fit forced through the origin of a plot of total FID area counts vs. mass of carbon spiked).
  - Each of the three analyses shows a percent recovery of 97 % to 103 % of theoretical ( $\mu$ gC measured/ $\mu$ gC spiked).
  - Each of the three analyses gives an FID response to the internal standard within 90 % to 110 % of the average FID response to the internal standard for the three calibration analyses.

- Each of the three analyses gives a response factor (counts/mgC) for the calibration standard that is within 90 % to 110 % of the average response factor for the three calibration analyses.

### **7.3.3 *Internal Standard***

The response factor (slope = counts/ $\mu\text{gC}$ ) from the three-point calibration with external standards (sucrose) and the area acquired for the internal standard (5 % methane in helium) for the calibrated and fixed-volume sample loop are both used to calculate the calibration constant ( $\mu\text{gC}$  per sample loop). An aliquot of the internal standard (5 % methane in helium) is injected near the end of each sample analysis and the acquired standard and sample area used to calculate the amount of OC and EC in the analyzed sample.

## **7.4 TOT Carbon Analyzer Procedure**

### **7.4.1 *Preanalysis Checklist***

1. Cylinders are checked for sufficient volume and pressure
2. Instrument gas flows are checked on the computer gas flow table.
3. The instrument pressure (psig) is checked prior to analysis (in the off-line mode it should be in the range 0.15–1 psi).

### **7.4.2 *Work Area Preparation***

1. In a designated area near the OC-EC instrument, an area which can be maintained free of clutter, dust, and chemicals is cleared. The area is covered with two to three layers of clean aluminum foil. The edges are taped down so that the foil is secured.
2. The punch, forceps, and aluminum foil are thoroughly cleaned with acetone at the beginning of each analytical session.

### **7.4.3 *Startup***

1. From standby, the CONTINUE button is pressed (if program has been exited, double clicking on the “OCECINST” icon will start the analyzer).
2. Set gas flow rates by slowly adjusting the corresponding needle valves on the instrument’s MFC box. Gas flow rates should be set as follows:

- He-1 set to 54–58 cc/min.
- He-2 set to 12–15 cc/min.
- He-3 set to 67–70 cc/min.
- He/O<sub>2</sub> set to 12–15 cc/min.
- Air set to 280–300 cc/min.
- Cal set to 10–14 cc/min.
- Hydrogen – when ready to ignite the flame in the FID, set the hydrogen flow to 80–100 cc/min. Once the flame has been lit (usually signaled by a small pop and can be confirmed with condensation on the forceps), return the flow rate to 40–59 cc/min.

**Caution:** Check the pressure (psig). In the off-line mode, it should be in the range 0.15–1 psi. While analyzing on-line, it should increase by approximately 1–2 psi. This oven pressure will change, depending on flow rates and resistance of the MnO<sub>2</sub> oxidizer bed and methanator oven.

3. Wait 20 min for the instrument to warm up and stabilize.
4. Under the Run menu select Clean Oven.
5. After the oven has been cleaned, recheck the flame and the flow rates of the gases before proceeding.

#### 7.4.4 *Running a Blank*

1. To run a blank, take a punch (1.5 cm<sup>2</sup>) from a prebaked (550 °C, 12 h) QFF using the manual precision punch. If the filters have not been baked, run the punch through the Clean Oven cycle before analyzing it as a blank. Handle punches with tweezers only.
2. Before loading a filter punch into the oven, make sure “*Safe to put in a new sample*” is displayed in the OC-EC software window. If there is a red bar displaying “*WAIT-Too hot (>75) for new sample*”, wait until the oven cools and the green bar appears.
3. Open the oven port. Be careful not to drop the rubber O-ring positioned between the oven port sections. Pull the sample holder out with forceps and place it on the support tray.
4. Place the filter punch on the sample holder using the stainless steel tweezers.

5. Steadily slide the sample holder and sample back into the oven with the forceps until it is stopped by the tip of the thermocouple. Then pull the sample holder forward slightly so it does not touch the thermocouple. Do not tip the sample holder from side to side or risk losing the sample in the oven port.
6. Close the oven port, making sure the O-ring sealed tightly and check the pressure reading on the monitor screen to make sure no warning flag appears (which would indicate a leak).
7. Enter Inst Blank 1 in the Sample ID # field. Enter the date in the file name of the Output Raw Data File block. Enter the value for Punch Area (1.5 cm<sup>2</sup>).
8. Click Start Analysis. Each run will take approximately 13 min.
9. To review the results, click the Shortcut to Calc2PD158 icon on the right side of the window and choose the correct file date.
10. Click Calculate First Sample. Total carbon (TC) for the blank ideally should be < 0.05 µg/cm<sup>2</sup>, although < 0.1 µg/cm<sup>2</sup> is also acceptable. If the result is higher, the blank filter punch must be reanalyzed.

#### **7.4.5 *Running Samples***

Quartz filters are stored in a freezer at -15 °C or below. An individual batch containing up to 50 filters may be kept in a refrigerator during analysis of that batch. Allow each Petri slide holder containing a quartz filter sample to warm to room temperature just before opening it to take a punch from the filter for analysis. Return the quartz filter to the Petri slide holder and the Petri slide holder to the refrigerator immediately after starting the analysis. Punches from filter samples should only be placed in the oven while the computer is in the “*Safe to put new sample*” mode.

1. To analyze punches from filter samples, perform steps 2 through 8 from Section 7.4.4. In step 7, enter the sample name in the Sample ID # field.
2. To review the results, click the Shortcut to Calc2PD158 icon on the right side of the window and choose the correct file date. Click Calculate First Sample, then calculate Next Sample to view the results for all analyzed samples.

#### **7.4.6 *Shutdown***

1. If intending to return to the analyzer later in the day or at some time over the next several days, the STANDBY box is clicked on. In STANDBY, the back oven and methanator oven will be maintained at a lower than normal operating temperature to increase heating coil life. Also the laser will be off and the pressure will be near zero, since there is very little flow.
2. If not intending to use the instrument for several days, EXIT is chosen from the file menu. This will turn off all power to the ovens, causing them to cool down. Gas flow rates are set as follows: H<sub>2</sub> set to 4–7 cc/min; Air set to off; Cal set to off; He-3 set to trickle flow at 6–8 cc/min; He-2 set to trickle flow at 0–4 cc/min; He-1 set to trickle flow at 6–8 cc/min; He/O<sub>2</sub> set to trickle flow at 4– cc/min.
3. When the program is being shut down for more than a few days, all gases should be turned off except for He-1 and He-3 (approximately 5–10 cc/min each).

## **8.0 DATA ACQUISITION, CALCULATIONS, AND DATA REDUCTION**

### **8.1 Blank Correction**

Final sample results should always be blank corrected. For that purpose, two types of blanks are used: laboratory and field blanks. The laboratory blank consists of the prebaked QFFs stored in the aluminum foil-lined Petri dishes in the laboratory. The field blank is a prebaked QFF subjected to all aspects of sample collection, transportation, field handling, and preservation as a real sample. Any measured OC and EC concentration in the blank samples represent contamination and should be deducted from the real samples.

### **8.2 Concentrations of Carbon Fractions on the Filter ( $\mu\text{gC}/\text{cm}^2$ )**

1. The software application used to run the analyzer (OCECInstxxx.exe) automatically stores data acquired during an analysis in comma-delimited ASCII text format for later computation, display, and printing.
2. Results are calculated using a second software application (OCECCalcxxx.exe) provided by Sunset Laboratory. The data for each sample can be printed in a graphic form (referred to as a thermogram) with temperature, laser transmittance and absorbance, and FID profiles. Text output on the thermogram includes calculated loadings of OC, EC, and TC. The uncertainty associated with the OC, EC, and TC measurements are also given on the thermogram. Other text outputs include EC/TC ratio, date, time,

calibration constant, punch area, FID1 and FID2 status, calibration area, split time, manual split time, initial absorbance, absorption coefficient of original elemental carbon, instrument name, analyst, laser correction factor, and transit time.

3. The calculation software application (OCECCalcxxx.exe) also creates a tab-delimited output file with additional data columns. In the output file, several header rows are followed by one row of data for each analysis. New rows are added to the bottom of the output file each time the calculation software is run, so the most recent calculations are always at the bottom of the file.

### 8.3 Recovery (%) of Sucrose Standards

Sucrose calibration standard ( $c = 0.421 \mu\text{g}/\mu\text{L}$ ) is run at the beginning of each day and a percent of recovery ( $\mu\text{gC}$  measured/ $\mu\text{gC}$  spiked) calculated as:

$$\% \text{ recovery} = \frac{m_{\text{tot}} (\mu\text{g}/\text{cm}^2) \times 1 \text{ cm}^2}{4.21 \mu\text{g}} \times 100 \%$$

where:  $m_{\text{tot}}$  is the total (OC + EC) carbon concentration measured ( $\mu\text{g}/\text{cm}^2$ ).

Acceptable % of recovery is from 93 % to 107 %.

### 8.4 Masses of Carbon Fractions on the Filter (in $\mu\text{gC}$ )

The mass (in  $\mu\text{gC}$ ) of OC, EC, and TC on the filter are calculated by multiplying the concentration ( $c$ ) of each type of carbon ( $\mu\text{gC}/\text{cm}^2$ ) by the deposit area ( $A$ ) of the filter in  $\text{cm}^2$ .

$$m = cA$$

NOTE: The filter deposit area is  $11.76 \text{ cm}^2$  for a 47-mm QFF used for sampling in a filter cassette with a 38.7-mm inside diameter, which defines the deposit area.

$$A = \pi r^2 = (3.14159) \left( \frac{38.7 \text{ mm} \left( \frac{1 \text{ cm}}{10 \text{ mm}} \right)}{2} \right)^2 = 11.76 \text{ cm}^2$$

The mass calculation of the OC, EC, and TC for the blanks (laboratory and field blanks) should be done using the same formulas. Carbon mass found in the blanks must be deducted from the carbon mass calculated for the field samples.

## 8.5 Concentrations of Carbon Fractions in Air

Sample volume is corrected to the EPA standard temperature and pressure (STP) conditions ( $T = 25\text{ }^{\circ}\text{C}$  and  $p = 760\text{ mm Hg}$ ). Mass ( $m$ , in  $\mu\text{g C}$ ) of each type of carbon on a filter can be divided by the STP volume ( $(V_{\text{air}})_{\text{STP}}$ ) of air sampled (in  $\text{m}^3$ ) to calculate concentrations ( $C_{\text{air}}$ ) of each type of carbon in the air sampled.

$$C_{\text{air}} = \frac{m}{(V_{\text{air}})_{\text{stp}}}$$

## 8.6 Measurement Uncertainty

Uncertainties of measurements for OC, EC, and TC, each of which contains both an absolute uncertainty and a relative uncertainty, are calculated by the data analysis software.

## 9.0 QUALITY CONTROL AND QUALITY ASSURANCE PROCEDURES

### 9.1 Thermocouple Temperature Calibration

The thermocouple temperature calibration procedure for the Sunset Laboratory analyzer is performed annually (earlier if needed) by trained staff or the APPCD Metrology Laboratory and according to instructions provided by Sunset. The OC-EC temperature calibration kit consists of the following: precision digital thermometer, NIST-traceable thermocouple, front oven interface hardware, serial cable, front oven heating coil, and new version of the software. Temperature offsets for target temperature ramps are implemented in the new version of the Sunset OC-EC software, and thus, when the software runs, the thermocouple will heat the zone in the filter area to match the required protocol (NIOSH 5040).

## 9.2 Calibration of Gas Flow Meters

A calibration is performed at least annually of the gas flow meters for the Sunset analyzer using APPCD Metrology Laboratory SOP FV-0235.1, which is included here by reference.

## 9.3 Instrument Blanks

An instrument blank for the Sunset analyzer is run using a punch from a precleaned QFF at the beginning of each day. An instrument blank must meet the following criteria:

- TC for the blank must be  $\leq 0.05 \mu\text{gC}/\text{cm}^2$ .
- The FID response to the internal standard injected at the end of the instrument blank analysis must be within 90 % to 110 % of the average FID response to the internal standard for the last (or current) three-point calibration.

If the instrument blank fails to meet either of the criteria above, determine if the problem is with the filter or with the instrument. If necessary, initiate corrective action to identify and solve any instrument problem before repeating the instrument blank analysis, which must be acceptable before continuing with analysis of other samples.

## 9.4 Calibrations

Calibration check samples of the Sunset analyzer are run at the beginning of each day, and a full three-point calibration is run at least once a week. Determine the minimum detection limit (MDL) for TC when the analyzer oven or methanator is changed or annually, whichever comes first.

**9.4.1** A complete set of calibration standards (i.e., three different mass loadings) is run at least once a week. If the least-squares correlation coefficient ( $R^2$ ) of area counts vs. total mass of carbon, force-fit through the origin (0,0), is not  $\geq 0.998$ , determine the cause of the nonlinearity, and initiate actions that will identify and solve any problem that might have arisen. Then the three-point calibration is repeated, which must yield satisfactory results before samples are analyzed. In addition, analysis of each of the three standards must meet all of the following criteria:

- The measured mass of total carbon for the calibration standard is within 93 % to 107 % of the true value.

- The FID response to the internal standard injected at the end of the calibration standard analysis is within 90% to 110% of the average FID response to the internal standard for all three calibration standard analyses.
- The response factor (counts/ $\mu\text{gC}$ ) for the calibration standard is within 90 % to 110 % of the average response factor for all three calibration standard analyses.

If any one of the sucrose standards analyses fails to meet any of the above criteria, repeat the analysis of that standard or, if necessary, initiate corrective action to solve the problem before analyzing samples.

**9.4.2** A sucrose standard calibration check sample is run after the initial instrument blank each day. The calibration check sample analysis results are valid if all of the following criteria are met:

- The measured mass of total carbon for the calibration check sample is within 93 % to 107 % of the true value.
- The FID response to the internal standard injected at the end of the calibration check sample analysis is within 90 % to 110 % of the average FID response to the internal standard for the last (or current) three-point calibration.
- The response factor (counts/ $\mu\text{gC}$ ) for the calibration check sample is within 90 % to 110 % of the average response factor for the last (or current) three-point calibration.

If the sucrose standard calibration check sample analysis fails to meet any of the above criteria, repeat the analysis of the standard or initiate corrective action, if necessary, to solve the problem before analyzing samples.

**9.4.3** At least three replicates of a low-level standard (0.421  $\mu\text{g}/\mu\text{L}$ ) are spiked on the quartz filter to determine the MDL for total carbon. The spike volume of that standard should be adjusted to have 5 times the estimated MDL which is 0.2  $\mu\text{g}/\text{cm}^2$ .

Determine the variance ( $S^2$ ) as follows:

$$S^2 = \frac{1}{n-1} \left[ \sum_{i=1}^n (x_i - \bar{x})^2 \right]$$

where  $x_i$  is the  $i$ th measurement of the variable  $x$  and  $\bar{x}$  is the average value of  $x$ .

Determine the standard deviation ( $s$ ) as follows:

$$s = (S^2)^{1/2}$$

Determine the MDL as follows:

$$MDL = t_{(n-1, \alpha = .99)}(s)$$

where  $t_{(n-1, \alpha = .99)}$  is the one-sided t-statistic appropriate for the number of samples used to determine ( $s$ ) at the 99 % level.

<u>No. of samples:</u>	<u>t-statistic</u>
3	6.96
4	4.54
5	3.75
6	3.36
7	3.14
8	3.00
9	2.90
10	2.82

If the MDL is  $\geq 0.5 \mu\text{gC}/\text{cm}^2$ , investigate the source of the problem and initiate corrective action, if necessary, to correct the problem, then repeat the MDL. An acceptable MDL must be obtained before samples can be analyzed.

## 9.5 Duplicate Sample Analysis

A duplicate punch is run approximately every tenth filter sample (at least 10 % of samples). Agreement between duplicate TC measurements depends on filter loading and the uniformity of the deposit. Acceptance criteria for duplicate

measurements at higher filter loadings ( $\geq 5 \mu\text{g}/\text{cm}^2$ ) are based on the relative percent difference (RPD) of the duplicate measurements, and the acceptance criterion for duplicate measurements at low filter loadings ( $< 5 \mu\text{g}/\text{cm}^2$ ) is based on absolute error ( $\pm 0.75 \mu\text{g}/\text{cm}^2$ ), which dominates the uncertainty of the TC measurement at low filter loadings. Acceptance criteria for the various concentration ranges are given in Table B-1.

**Table B-1. Acceptance Criteria**

Total Carbon Concentration Range	Acceptance Criterion
Values greater than $10 \mu\text{g}/\text{cm}^2$	Less than 10% RPD
5-10 $\mu\text{g}/\text{cm}^2$	Less than 15% RPD
Values less than $5 \mu\text{g}/\text{cm}^2$	Within $0.75 \mu\text{g}/\text{cm}^2$

As stated above, nonuniform filter deposit can cause a difference between duplicate measurements. If the deposit on a filter appears visually to be nonuniform or if a duplicate analysis is run and the duplicate measurements fail the appropriate acceptance criterion in the table above, flag the analysis data for that filter as “Nonuniform Deposit.”

## 9.6 FID Response to Internal Standard

If the Sunset analyzer FID response to the internal standard for any sample analysis run on a given day is outside the range 95–105 % of the average response for all samples run that day, discard the results of that analysis and, if necessary, repeat the analysis with a second punch, if available, from the same filter.

NOTE: An FID response significantly lower than the average occurs when the ball joint at the front of the instrument leaks during the run.

## 9.7 Transit Time

During TOT analysis, the laser signal monitors the transmittance of the filter in real time while FID response to carbon evolved from the filter lags behind because of the time required for gaseous carbon species to travel from the filter to the FID. This lag time is called the transit time. The transit time is used by the calculation software to align FID response properly with laser transmittance for calculation of OC and EC fractions (by integration of FID response) based on the OC-EC split time (which is determined solely from the laser transmittance). A new transit time must be determined whenever the effective volume of the analysis system between the oven and the FID changes. Such changes include

replacement of the oven, replacement of the methanator tube, replacement of the FID, and replacement or modification of any transfer line between the oven and the FID.

## 9.8 Control Charts

Control charts are used to show performance of the Sunset analyzer over time.

1. Measured TC for all instrument blanks by date is plotted.
2. Linearity ( $R^2$ ) of three-point calibrations by date is plotted.
3. Percent recovery for low, mid-level, and high calibration standards as well as average percent recovery for each three-point calibration by date is plotted;  $\pm 10$  % bars for average percent recovery are shown.
4. FID response factors for TC for each three-point calibration by date are plotted. Response factors measured for each standard (to show range) and the average response factor for all three standards (to show mean) are plotted.
5. Percent recovery for all daily calibration checks by date is plotted.
6. Relative percent difference of duplicate measurements versus average measured TC for all duplicates is plotted.

## 9.9 Laser Transmittance

Laser reading (displayed in raw data files under the heading “laser”) is an important indicator not only of EC loading on the filter punch but also of the condition of the quartz optical flats used for the boat and for the upper and lower windows of the quartz oven.

1. A laser reading  $< 1,000$  for a filter punch at the beginning of an analysis indicates a fairly heavy loading of EC in the sample and provides a warning that the OC-EC split point set by the software could be inaccurate because the laser response might “bottom out” during the char-forming, non-oxidizing heating ramp. The absorbance plot on the bottom of the printed thermogram can be used to check the split point.
2. An initial laser reading  $\geq 3,000$  for a clean filter punch and a series of final laser readings that drift slightly upward during the last seconds of an analysis (as the oven cools) generally indicate that the quartz optical flats (boat and oven windows) are adequately free of frosting for an accurate assignment of the OC-EC split. If the initial laser reading is  $< 3,000$  or if the laser reading drifts slightly downward during the last seconds of an analysis (as the oven

cools), the quartz optical flats (boat and oven windows) should be inspected for frosting and the boat (either oven or both) replaced, if necessary.

### 9.10 Balance Calibration

Balance performance verification must be performed at the following frequency:

- At least once a year by the APPCD Metrology Laboratory.
- Before weighing any filter by zeroing and spanning the balance with at least one calibration weight.
- Before and after filter weighing sessions by weighing reference PM sample filters.

## 10.0 REFERENCES AND SUPPORTING DOCUMENTATION

National Institute of Occupational Safety and Health. (2003). Diesel particulate matter (as elemental carbon). Method 5040, Issue 3, available at:  
<http://198.246.98.21/niosh/nmam/pdfs/5040.pdf>.

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OC/EC Analyzer Calibration and Analysis Procedures, MOP 2511, May 2009.

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Standard Operating Procedure for the Determination of Organic, Elemental, and Total Carbon in Particulate Matter using a Thermal/Optical–Transmittance Carbon Analyzer. (2004). Center for Air Resources, Engineering and Science (CARES), Clarkson University, Potsdam, New York, May 10, 2004.

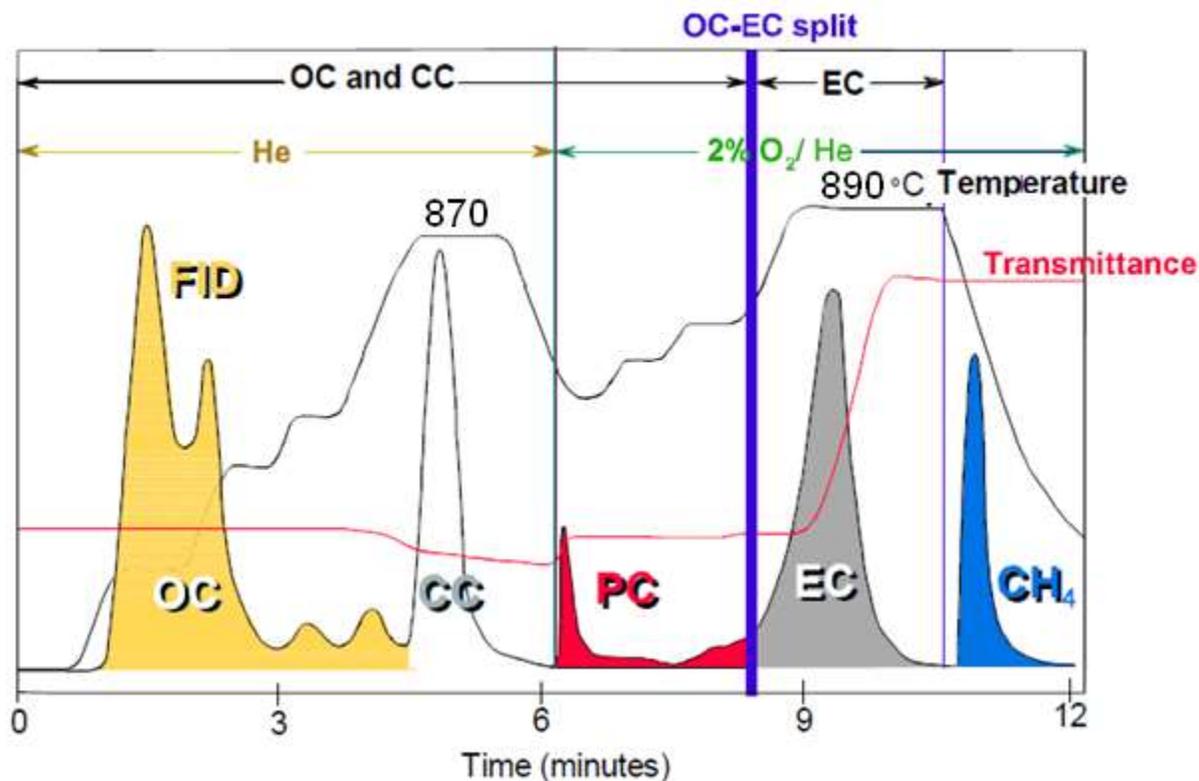
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Procedure for Calibration of a Mass Flow Controller (MFC) Using a Gilibrator<sup>®</sup>, MOP FV-0237.0. (2010). U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, Research Triangle Park, NC.

Procedure for Calibration of Gas Flow Meters of the Sunset Lab Elemental Carbon/Organic Carbon Analyzer Using a Gilibrator<sup>®</sup>, MOP FV-0235.1. (2008). U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, Research Triangle Park, NC.

## 11.0 ATTACHMENTS

### 11.1 Example Thermogram for Filter Sample



Thermogram for filter sample containing organic carbon (OC), carbonate carbon (CC), and elemental carbon (EC). Pyrolytically generated carbon is represented here as (PC). The final peak is the methane (CH<sub>4</sub>) calibration peak. (Figure from NIOSH 5040 method: Issue 3, 1999.)

## 11.2 Temperature Profile for the NIOSH 5040 Method

CARRIER GAS	TEMP. (°C)	RAMP RATE (°C/s)	RESIDENCE TIME (s)	CARBON FRACTION
Helium	310	4	70	OC1
Helium	475	8	60	OC2
Helium	615	10	60	OC3
Helium	870	8	105	OC4
98% Helium/2% Oxygen	550	9	60	EC1
98% Helium/2% Oxygen	625	10	60	EC2
98% Helium/2% Oxygen	700	12	60	EC3
98% Helium/2% Oxygen	775	13	60	EC4
98% Helium/2% Oxygen	890	8	110	EC5
CalibrationOx	1		110	

# Appendix C: Development of an Improved Multi-angle Absorption Photometer (SuperMAAP)



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## 1.0 INTRODUCTION

The Thermo Fisher Scientific (Waltham, MA, USA) Model 5012 MAAP is a commercially available, filter-based absorption photometer that deposits aerosol onto a 2 cm<sup>2</sup> area on a quartz-fiber filter (QFF) tape. A 630-nm (670-nm nominal value) wavelength light-emitting diode (LED) illuminates the area, and multiple photodetectors measure the transmission and scattering/reflection of the light from the depositing aerosol layer and the underlying filter. Figure C-1 (Petzold et al., 2005) shows a schematic diagram of the MAAP and the position of the optical sensors. A two stream, radiation transfer calculation is used to separate the light absorption by the aerosol layer from the scattered light from the particles and filter matrix. Figure C-2 (Petzold et al., 2005) shows the radiation processes within the MAAP. A narrow range of mass absorption coefficients,  $\sigma_{abs} \sim 6.4\text{--}6.6 \text{ m}^2/\text{g}$ , is reported to provide a decent fit between measured absorption coefficients and collocated particle mass measurements for commercially produced soot particles and urban particles containing refractory carbon soot collected at several sites. The standard 5012 MAAP is designed to be operated with a flow rate of 8–24 L/min and provides measurements of particulate absorption and black carbon (BC) mass loadings on the time scale of 1, 10, and 30 min. The MAAP is a self-contained instrument and therefore provides a firmware-determined measurement of the BC mass loadings on a small LED screen on the front panel. Access to this processed data is provided using several serial port data output formats. Detailed descriptions of the standard MAAP are provided in a number of publications such as Petzold et al. (2002, 2005).

A number of research organizations including Aerodyne Research, Inc. (ARI), United Technologies Research Center (UTRC), National Aeronautics and Space Administration (NASA)-Langley, and the U.S. Environmental Protection Agency (EPA) National Risk Management Research Laboratory (NRMRL) have used the Thermo 5012 MAAP to measure BC emissions from aircraft turbine engines. Since the MAAP was originally designed for ambient applications, several modifications have been made to the standard instrument. ARI has implemented the most advanced of these modifications. Working with Andreas Petzold, formerly of the German Aerospace Center, and Kevin Goohs from Thermo Fisher Scientific, ARI started using a rapid ( $\sim 1 \text{ s}$ ) data collection protocol and developed a data analysis routine within the WaveMetrics Inc. (Tigard, OR, USA) IgorPro platform. ARI's extensive laboratory and field work experience with the MAAP has allowed them to identify and address specific instrument-related issues and develop various sampling protocols that enable rapid, accurate measurements to be made with the MAAP for a wide range of sampling conditions.

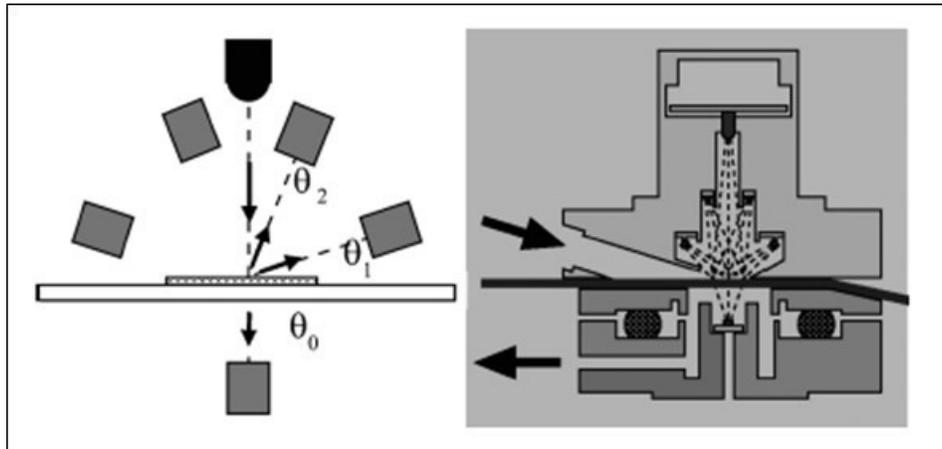


Figure C-1. Optical sensor of the MAAP. Left: position of photodetectors at detection angles  $\theta_0 = 0^\circ$ ,  $\theta_1 = 130^\circ$ , and  $\theta_2 = 165^\circ$  with respect to the incident light beam ( $\lambda_{\text{MAAP}} = 670 \text{ nm}$ ). Right: Layout of the MAAP sensor unit with arrows indicating the airflow through the sensor unit across the filter tape.

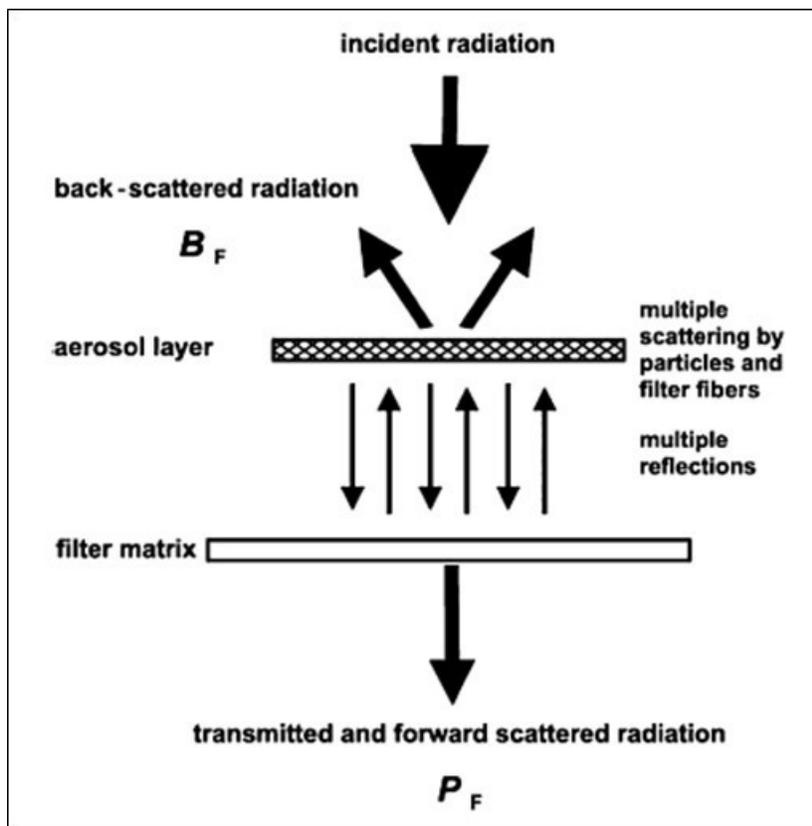


Figure C-2. Schematic representation of radiation process to be considered in the two-layer system consisting of an aerosol-loaded filter layer and the particle-free filter matrix.

However, further work was needed to make the instrument truly useful for source monitoring applications such as aircraft turbines. Therefore, EPA initiated a separate research effort to develop an improved version of the MAAP instrument that would be both useful and user-friendly. In this effort, the goal was to keep the basic instrument the same as that offered for purchase by Thermo Fisher Scientific but to add whatever hardware and software is needed to make it more suitable for use during engine certification. This appendix describes the modifications made to the standard 5012 MAAP, called the “SuperMAAP,” under the EPA program.

## **2.0 INSTRUMENT REQUIREMENTS**

As a starting point, EPA organized a workshop to discuss the goals and objectives of the research and to develop specifications for the modified instrument. Workshop participants included Andreas Petzold, inventor of the MAAP, and representatives from ARI, UTRC, and EPA. An outside contractor took detailed minutes to allow free discussion by the workshop participants. These detailed minutes were then used as the starting point for the SuperMAAP development process.

During the workshop, the participants agreed on several key objectives for the SuperMAAP to be of use in engine certification environments:

- Reduce flow through the filter tape to extend the time between filter changes.
- Isolate the MAAP from the main sampling line during filter changes.
- Perform the necessary calculations to determine BC concentration on a 1-Hz basis and log the data.
- Calculate appropriate statistics from the calculated BC concentrations.
- Provide the ability to manually implement a filter change.
- Monitor the light transmission percentage in real time so that the operator can determine when an automatic filter change is about to take place.
- Allow for and document some type of quality control (QC) check to tell the operator the instrument is working properly and ready for use.
- Develop an add-on “package” that incorporates all necessary changes for use in certification environments.

To meet these objectives, additional hardware and software were identified. With respect to new hardware, a “box on the box” concept was developed to avoid making any physical modifications to the standard MAAP instrument. The specific hardware changes were to add two mass flow controllers (MFCs), filters, an automated three-way valve, and an isokinetic sampler to the instrument inlet; supply a new sample pump not controlled

by the instrument firmware; and provide a new data acquisition board and DC power supply for use by the new operating software.

Regarding the new software, the workshop participants decided that code written within the National Instruments (Austin, TX, USA) LabView platform would be most appropriate for this application. The LabView code would be prepared by an outside firm most familiar with the subtle nuances required by the ARI data analysis scheme. The following requirements were established for the new LabView code:

- Process and log the 1-Hz data stream from the RS-232 output.
- Allow the operator to set the flows below 8 L/min to extend filter life.
- Automatically operate the three-way valve to isolate the instrument from the main sample line during filter changes.
- Continuously monitor filter life (percent transmission) and provide the capability to manually change the filter tape to a new spot.
- Provide a real-time display of the data being generated.
- Document QC parameters from the instrument to verify proper operation.
- Generate spreadsheet files of both the raw and processed data.

As part of the new LabView software, a conceptual graphical user interface (GUI) was also developed during the workshop. This GUI was designed to be user-friendly and specifically tailored for use during engine certification. Basically, the GUI would allow the user to start and stop data acquisition for each power condition being tested with the average concentration of BC and summary statistics available immediately at completion of the measurements. In addition, the code should also be open source so that it is accessible to anyone wanting to build a SuperMAAP through a software request to EPA.

### **3.0 HARDWARE MODIFICATIONS**

The hardware modifications identified during the workshop that were added to the standard 5012 MAAP are shown schematically in Figure C-3. The external hardware is mounted in a 42- × 44.5- × 40.6-cm light-gauge aluminum enclosure mounted on the top plate of the standard 5012 MAAP. The flow path for the SuperMAAP was plumbed as shown in Figure C-3. Photos of the SuperMAAP including the hardware mounting arrangement are provided in Figure C-4, with a complete parts list shown in Table C-1 and wiring diagrams in Figures C-5 through C-9.

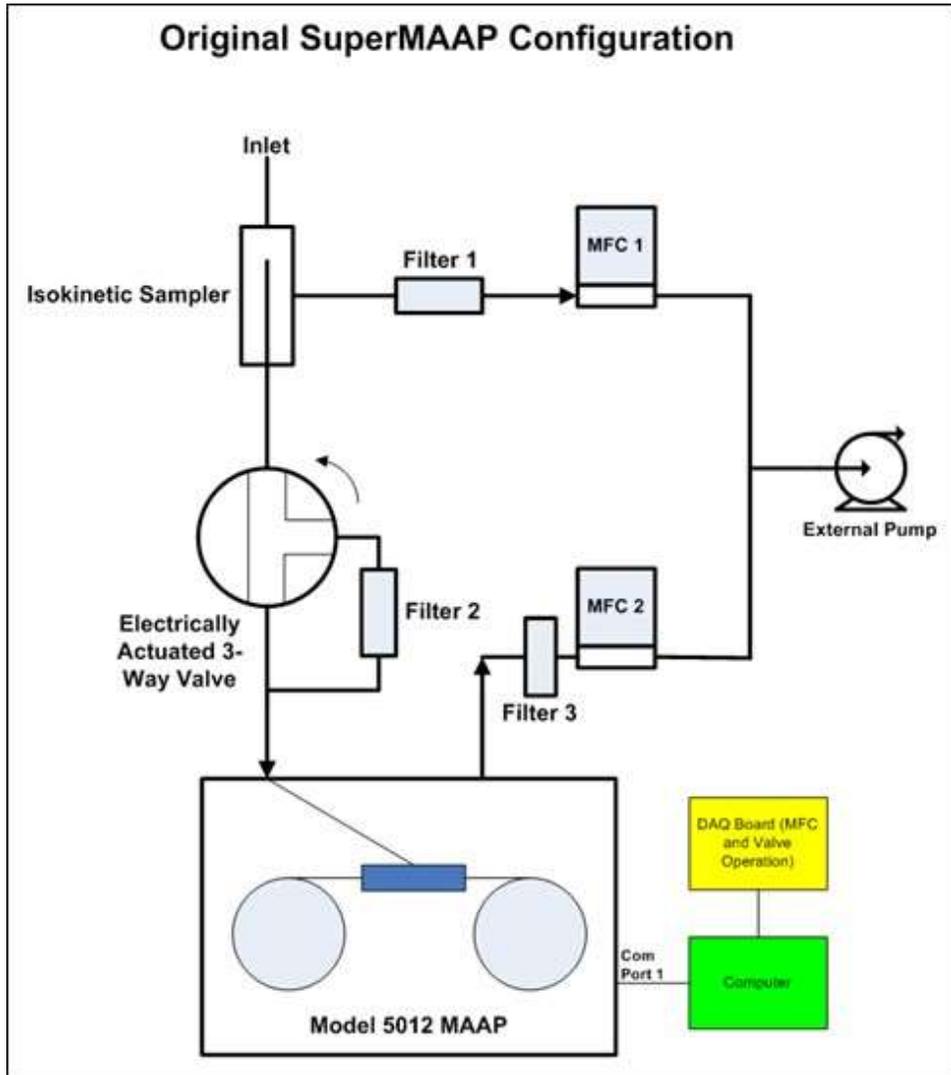


Figure C-3. Schematic of SuperMAAP hardware additions and signal processing as developed from user workshop.



**Figure C-4. Front and back views of the SuperMAAP showing original hardware configuration based on workshop discussions.**

**Table C-1. SuperMAAP Parts List**

<b>Vendor</b>	<b>Manufacturer Part Number</b>	<b>Description</b>	<b>Quantity</b>
MKS Instruments, Andover, MA, USA	M100B01353CS1BV	M100B Mass-Flo economical, analog, elastomer-sealed MFC	1
MKS Instruments, Andover, MA, USA	M100B01324CS1BV	M100B Mass-Flo economical, analog, elastomer-sealed MFC	1
National Instruments, Austin, TX, USA	781424-01	cDAQ-9188, CompactDAQ chassis (8-slot ENET)	1
National Instruments, Austin, TX, USA	779018-01	NI 9915 DIN rail kit for 8-slot chassis	1
National Instruments, Austin, TX, USA	763000-01	Power cord, AC, US, 120 V AC, 2.3 meters	1
National Instruments, Austin, TX, USA	763068-01	Power cord, 240V, 10A, North American	1
National Instruments, Austin, TX, USA	779002-01	NI 9421 8-channel 24V 100 US, sinking digital input module	1
National Instruments, Austin, TX, USA	779012-01	NI 9263 4-channel +- 10V, 100 kS/s per channel, 16-bit analog output module	1
National Instruments, Austin, TX, USA	779013-01	NI 9201 8-channel +- 10V, 500 kS/s per, 12-bit analog input module	1
Automation Direct, Cumming, GA, USA	FC-33	Signal conditioner, isolator, IN: mA, V / OUT: mA, V	1
Automation Direct, Cumming, GA, USA	DN-G4	Terminal block; wire-to-wire; screw-cage; 6; 9 mm; polyamide 6.6; green/yellow	1
Automation Direct, Cumming, GA, USA	DN-D10X	Multi-level clamp terminal block gray, 18-10AWG	14
Automation Direct, Cumming, GA, USA	NON-1/2	250 V AC, 0.5 A fuse, general purpose	2
Automation Direct, Cumming, GA, USA	NON-15	250 V AC, 15 A fuse, general purpose	1
Automation Direct, Cumming, GA, USA	DN-F10L110	Fuse holder terminal block	3
Automation Direct, Cumming, GA, USA	PSE15-215	±15VDC 15W power supply	1
Automation Direct, Cumming, GA, USA	PSE24-130	24VDC 30W power supply	1
Indus. Automation Components, London, ON, Canada	Valworx 563303	Stainless steel 3-way valve	1
Indus. Automation Components, London, ON, Canada	Valworx 588125	Wall bracket kit	1
Pall Life Sciences, Port Washington, NY, USA	12144	HEPA capsule filter	2
Parker Hannifin Corporation, Greensboro, NC, USA	9922-11-AAQ	DFU grade AAQ filter	2
Swagelok, Wake Forest, NC, USA	SS-400-2-4	90° elbow, 1/4-in. NPT to 1/4-in. tube	4
Swagelok, Wake Forest, NC, USA	SS-400-3	1/4-in. union tee	3
Swagelok, Wake Forest, NC, USA	SS-1010-3	5/8-in. union tee	1
Swagelok, Wake Forest, NC, USA	SS-400-R-10	1/4-in. to 5/8-in. reducer	2
Swagelok, Wake Forest, NC, USA	SS-400-1-4	1/4-in. NPT to 1/4-in. tube male connector	2
Swagelok, Wake Forest, NC, USA	SS-400-9	1/4-in. 90° union elbow	2
Swagelok, Wake Forest, NC, USA	SS-400-3-4TMT	1/4-in. run tee	1
Swagelok, Wake Forest, NC, USA	SS-1010-6-6	5/8-in. to 3/8-in. reducing union	1
Swagelok, Wake Forest, NC USA	SS-1210-6-6	3/4-in. to 3/8-in. reducing union	1

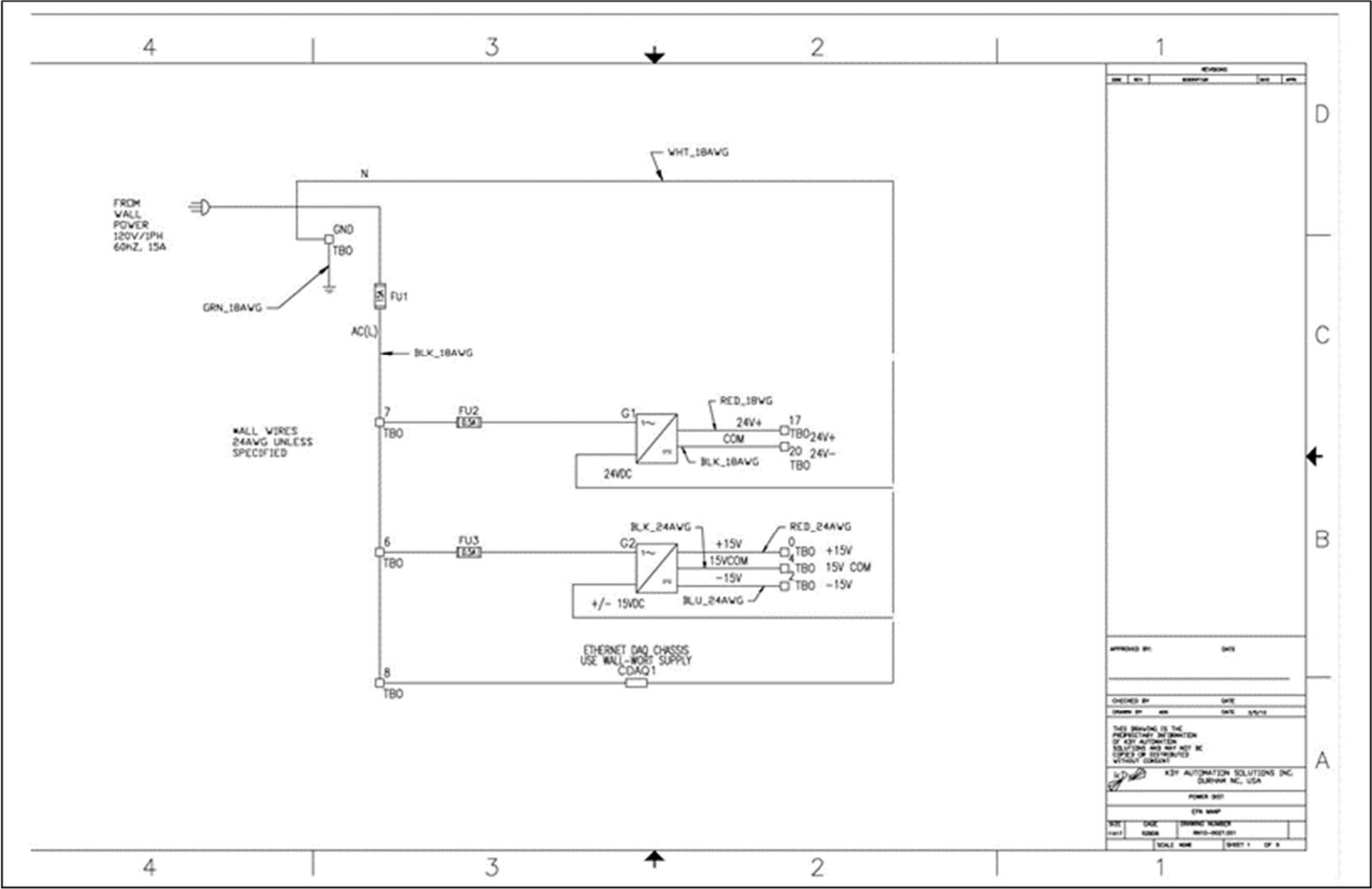


Figure C-5. Wiring diagram for Ethernet data acquisition chassis.

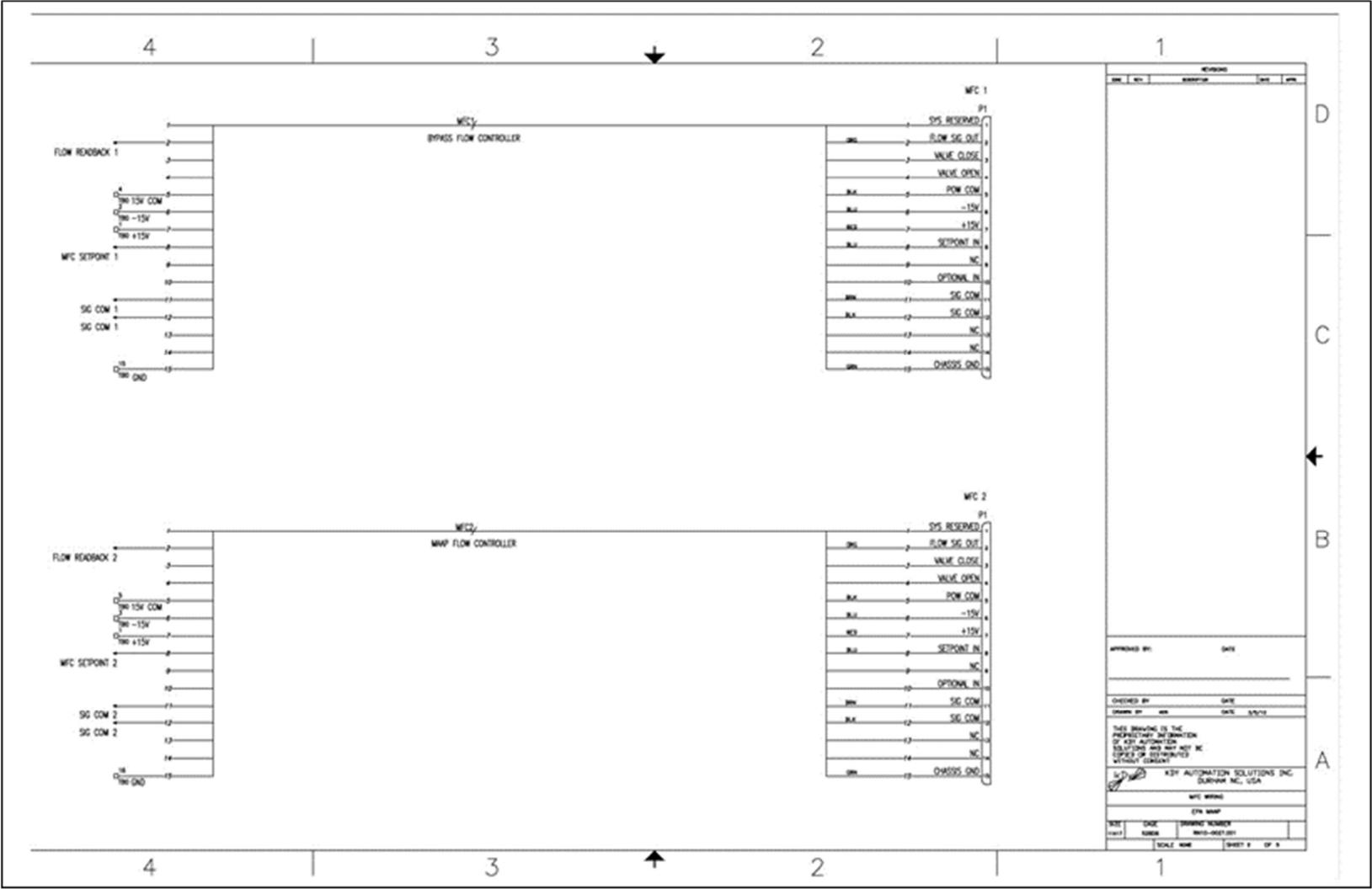


Figure C-6. Wiring diagram for MFC wiring.

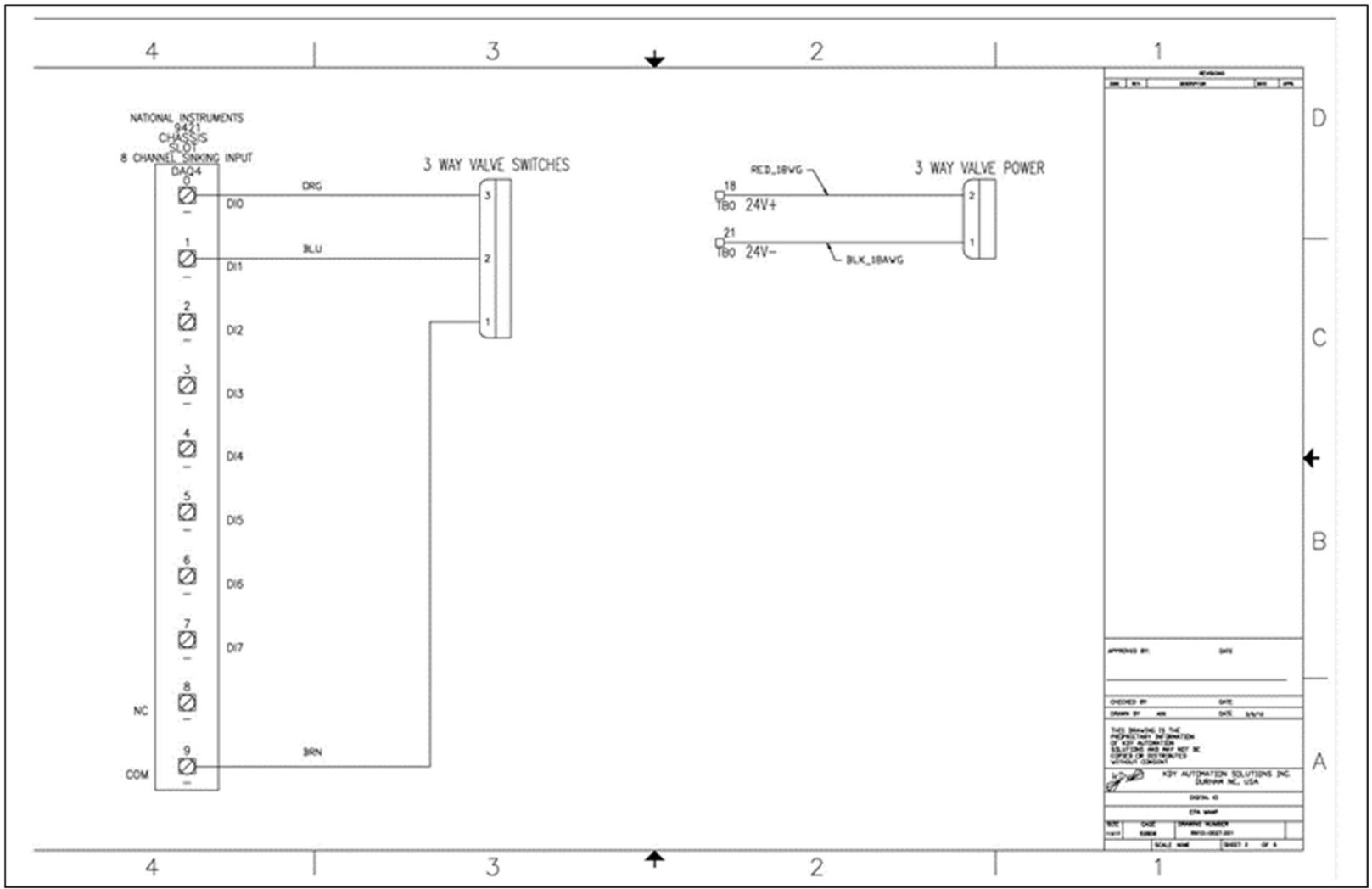


Figure C-7. Wiring diagram for digital input/output.

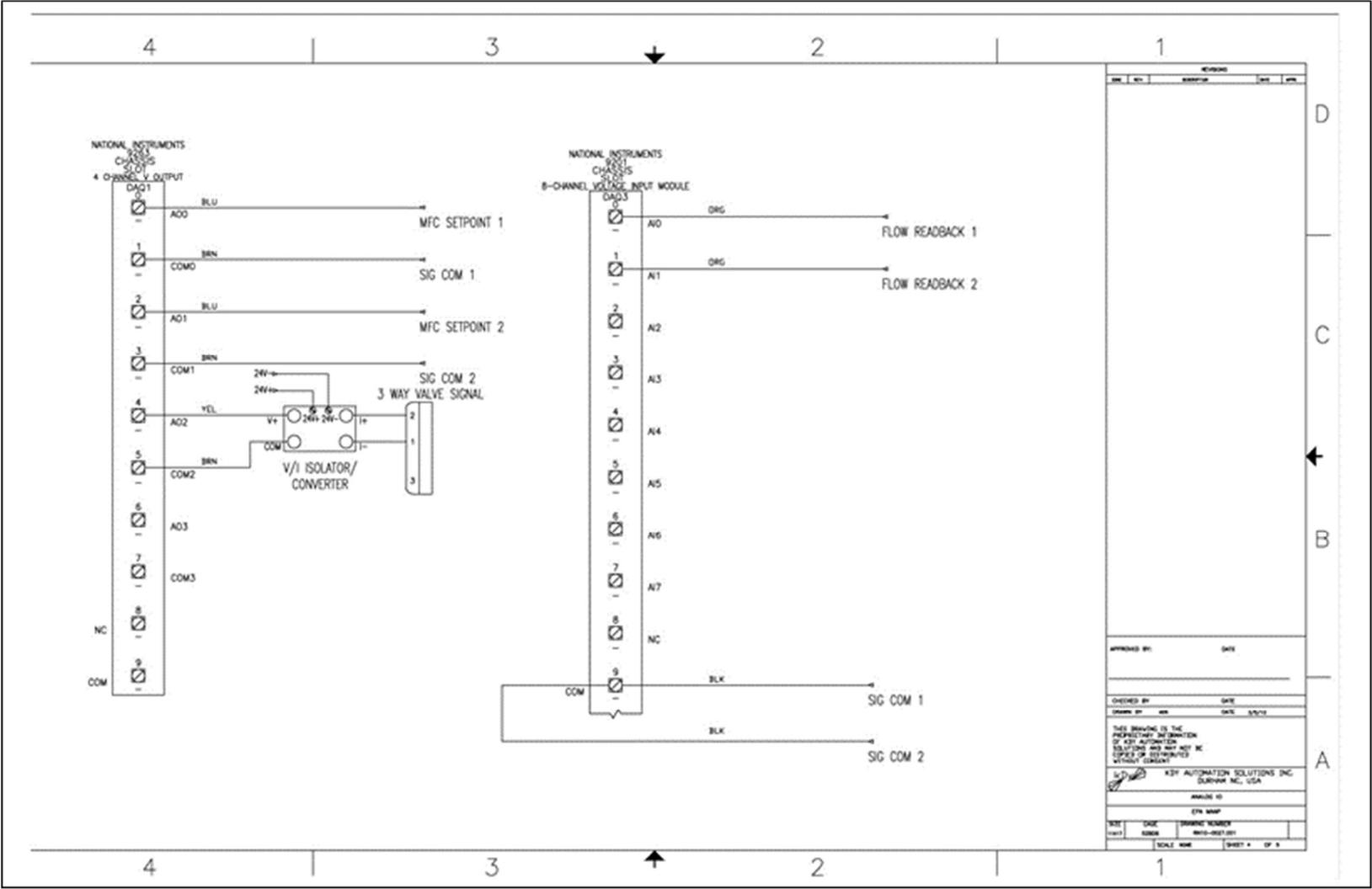


Figure C- 8. Wiring diagram for analog input/output.



As shown in Figure C-3, the sample enters the top of the instrument through a 9.5-mm outside diameter (OD) stainless steel sampling line. Upon entering the instrument, a subsample of the flow is extracted by an isokinetic probe inserted into a bored-through 16-mm OD stainless steel tee. The excess flow then passes through a filter and bypass line to an MFC and then the pump. The subsample flow is directed straight through an electrically operated, three-way, full-flow ball valve to the sensor head of the instrument. After the flow penetrates the filter tape and exits the analyzer, the flow is then directed to a second MFC and the external pump.

During automatic tape changes, the head sensor opens and the three-way valve goes to bypass mode and directs air in-leakage from the open head through a filter to avoid contaminating the sample flow of any other analyzers on the same sampling line. It was discovered that this scheme *did not* isolate the instrument from the other instruments on the same line. Instead, when the three-way valve activates and the tape head opens up, the software stops the flow through the instrument, allowing laboratory air to enter the system through the optical sensor head and cause a pressure fluctuation for the other instruments. Therefore, a data correction scheme (described in 6.0) was needed along with hardware/software changes to address the problem. EPA is currently working on modifications to the original configuration that will be reported in detail in a later publication.

#### 4.0 SOFTWARE DEVELOPMENT

As stated previously, new LabView code was written specifically for operation of the SuperMAAP. The code runs independently of the standard 5012 MAAP firmware but uses the firmware's raw output as input to calculate MBC and CBC much faster than 1 min as in the standard instrument. The new LabView code was based on the calculation scheme developed previously by ARI for their IgorPro program. This calculation scheme is described below.

Basically, two energy balance equations (taken from Petzold and Schönlinner, 2004) need to be solved simultaneously to derive the MBC on the filter and the CBC in the sampled air:

$$\frac{P_F}{P_F^{(0)}} = \frac{T_L + F_L}{1 - B_L^* B_M} \quad (\text{C-1a})$$

$$\frac{B_F}{B_F^{(0)}} = P_L^* \frac{T_L + F_L}{1 - B_L^* B_M} + \frac{B_L}{B_M} \quad (\text{C-1b})$$

#### Notation

Variables:

F = fraction of forward-scattered radiation

B = fraction of back-scattered radiation

T = fraction of transmitted radiation

P = total fraction of radiation passing through a layer,  $P = T + F$

Subscripts:

L = particle-loaded aerosol filter layer

M = particle-free filter matrix

F = composite system consisting of aerosol-filter layer and particle-free filter matrix

Superscripts:

(0) = property referring to a blank filter sample

No superscript = particle-loaded filter sample

\* = illumination by diffuse radiation

Left-Hand Side

The left-hand side of the equations above is a function of the “signal” data as follows:

$$P_F = 2S(\theta = 0) \tag{C-2}$$

$$B_F = S(\theta = \pi) \left[ 2\alpha + (1 - \alpha)\sqrt{2\pi} \rho \right] \tag{C-3}$$

Therefore:

$$\left( \frac{P_F}{P_F^{(0)}} \right) = f(S(\theta = 0)) \tag{C-4}$$

$$\left( \frac{B_F}{B_F^{(0)}} \right) = f(S(\theta = \pi), \alpha, \rho) \tag{C-5}$$

where  $\alpha$  is the fraction of diffusely scattered radiation and  $\rho$  is filter surface roughness.

$$S(\theta) \propto \left( \alpha \cos(\theta - \pi) + (1 - \alpha) \exp \left[ -\frac{1}{2} \frac{(\theta - \pi)^2}{\rho^2} \right] \right) \quad (\text{C-6a})$$

$$\frac{S(\theta = 130^\circ)}{S(\theta = 165^\circ)} = 0.2984 + 0.4064\alpha \quad (\text{C-6b})$$

where  $\theta = 130^\circ$  was used in theory, but  $\theta = 135^\circ$  was used in practice and actual calculations below.

### Right-Hand Side

The right-hand side of the main equations consists of nonlinear functions of two unknowns,  $\tau_L$  and  $SSA_L$ . There are two equations and two unknowns as follows:

$$RHS_{(1a)} = f(\tau_L, SSA_L; g) \quad (\text{C-7a})$$

$$RHS_{(1b)} = f(\tau_L, SSA_L; g) \quad (\text{C-7b})$$

where:

$\tau_L$  = optical depth of aerosol-filter layer

$SSA_L$  = single-scattering albedo of aerosol-filter layer

$g$  = aerosol asymmetry parameter

## **4.1 Mass of Black Carbon on Filter (unit conversions not shown)**

The MBC is calculated by:

$$MBC = (1 - SSA_L) \frac{\tau_L}{\sigma_{abs}} A \quad (\text{C-8})$$

where:

MBC = mass of black carbon (ng) on particle-loaded filter

$\sigma_{abs}$  = aerosol absorption coefficient ( $\text{m}^2/\text{g}$ )

A = active filter surface area (m<sup>2</sup>)

#### 4.2 Concentration of Black Carbon

The CBC is calculated using Equation C-9.

$$\text{CBC} = \Delta\text{MBC}/\text{Sample Flow} = \Delta\text{MBC}/\Delta V \quad (\text{C-9})$$

where:

$\Delta\text{MBC}$  = difference in mass of black carbon (ng) on particle-loaded filter between time 1 ( $t_1$ ) and time 2 ( $t_2$ )

$\Delta V$  = difference in the volume of air sampled during measurement (m<sup>3</sup>) between  $t_1$  and  $t_2$

t = clock time

such that CBC is the change in the MBC in time divided by the flow (i.e., change in sample volume in time).

#### 4.3 Measured Aerosol Absorption Coefficient (Mm<sup>-1</sup>)

The aerosol absorption coefficient ( $B_{abs}$ ) is calculated by:

$$B_{abs} = \text{CBC} * \sigma_{abs} \quad (\text{C-10})$$

where

CBC = mass concentration of black carbon in sample air (μg/m<sup>3</sup>)

$\sigma_{abs}$  = assumed mass-specific absorption coefficient (6.6 m<sup>2</sup>/g)

Note that  $B_{abs}$  is the more fundamental calculation (compared with CBC) as it relies on measured MAAP signals but does not require an assumed mass-specific absorption coefficient. The direct calculation of  $B_{abs}$  is as follows:

$$B_{abs} = (1 - \text{SSA}_L) \frac{A}{V} \tau_L \quad (\text{C-11})$$

where:

$\tau_L$  = optical depth of aerosol-filter layer

$\text{SSA}_L$  = single scattering albedo of aerosol-filter layer

A = active filter surface area (m<sup>2</sup>)

V = volume of air sampled during measurement (m<sup>3</sup>)

#### 4.4 LabView Code

The calculation scheme above was implemented in LabView using the RS-232 output from the 5012 MAAP firmware Version 1.29. The output from the firmware is as follows with an “a\_” prefix indicating signal for particle loaded filter, a “b\_” prefix indicating signal for blank filter after filter change, and a “c\_” prefix indicating dark current readings:

*Maap Date, Maap Time, Maap Flow, a\_sref, a\_szero, a\_s135, a\_s165,  
 b\_sref, b\_szero, b\_s135, b\_s165, c\_sref, c\_szero, c\_s135, c\_s165,  
 CBC\_thermo, MBC\_thermo, T1, T2, T4, P1, P3, Volume,  
 HeizRegel\*0.2443*

The left-hand side calculations for equations C-1a and C-1b above use only measured signals from raw data. The calculations of normalized signals, S<sup>(0)</sup> and S, as a function of angle (Θ = 0, 135, and 165°) are:

$$S^{(0)}(\Theta = 0) = (b\_szero - c\_szero)/(b\_sref - c\_sref)$$

$$S^{(0)}(\Theta = 135) = (b\_s135 - c\_s135)/(b\_sref - c\_sref)$$

$$S^{(0)}(\Theta = 165) = (b\_s165 - c\_s165)/(b\_sref - c\_sref)$$

$$S(\Theta = 0) = (a\_szero - c\_szero)/(a\_sref - c\_sref)$$

$$S(\Theta = 135) = (a\_s135 - c\_s135)/(a\_sref - c\_sref)$$

$$S(\Theta = 165) = (a\_s165 - c\_s165)/(a\_sref - c\_sref)$$

The calculation of the fractions of radiation transmitted, P, and reflected, B, from filter layers (blank and particle-loaded filters) for a blank filter are then:

$$\alpha^{(0)} = (S^{(0)}(\Theta = 135)/S^{(0)}(\Theta = 165) - 0.2984)/0.4064$$

$$\text{const1} = \alpha^{(0)} * \text{COS}(165.0 * \pi / 180.0 - \pi)$$

$$\text{const2} = (1.0 - \alpha^{(0)}) * \text{EXP}(-0.5 * (((165.0 * \pi / 180.0 - \pi)/\rho)^2.0))$$

$$S^{(0)}(\Theta = \pi) = S^{(0)}(\Theta = 165)/(\text{const1} + \text{const2})$$

$$P^{(0)}_F = 2.0 * S^{(0)}(\Theta = 0)$$

$$B_F^{(0)} = S^{(0)}(\Theta = \pi) * (2.0 * \alpha^{(0)} + (1.0 - \alpha^{(0)}) * \text{SQRT}(2.0 * \pi) * \rho)$$

and for a particle loaded filter:

$$\alpha = (S(\Theta = 135)/S(\Theta = 165) - 0.2984)/0.4064$$

$$\text{const1} = \alpha * \text{COS}(165.0 * \pi/180.0 - \pi)$$

$$\text{const2} = (1.0 - \alpha) * \text{EXP}(-0.5 * (((165.0 * \pi/180.0 - \pi)/\rho)^{2.0}))$$

$$S(\Theta = \pi) = S(\Theta = 165)/(\text{const1} + \text{const2})$$

$$P_F = 2.0 * S(\Theta = 0)$$

$$B_F = S(\Theta = \pi) * (2.0 * \alpha + (1.0 - \alpha) * \text{SQRT}(2.0 * \pi) * \rho)$$

Calculation of the normalized transmission, TRANS, and reflection, REF, are then:

$$\text{TRANS} = P_F/P_F^{(0)}$$

$$\text{REF} = B_F/B_F^{(0)}$$

Rearranging equations C-1a and C-1b (subtracting TRANS and REF from both sides) and solving the two equations for two unknowns ( $\tau_L$  and  $SSA_L$ ) yields:

$$0 = \frac{T_L + F_L}{1 - B_L^* B_M} - \frac{P_F}{P_F^{(0)}} \quad (\text{C-1a}^*)$$

$$0 = P_L^* \frac{T_L + F_L}{1 - B_L^* B_M} + \frac{B_L}{B_M} - \frac{B_F}{B_F^{(0)}} \quad (\text{C-1b}^*)$$

These calculations for equations C-1a\* and C-1b\* use the following parameters in the code:

$$\text{Filter roughness } (\rho) = 0.50$$

$$\text{Asymmetry factor } (g) = 0.75$$

$$\text{Active filter area } (A) = 2 \times 10^{-4} \text{ m}^2$$

$$\text{Mass specific absorption coefficient } (\rho_{abs}) = 6.6 \text{ m}^2/\text{g}$$

$$\text{Fraction of radiation backscattered from particle-free filter matrix } (B_M) = 0.70$$

Initial guess for  $\tau_L$  (total optical depth of particle-loaded aerosol-filter layer) = 2.5

Initial guess for  $SSA_L$  (single scatter albedo of loaded aerosol-filter layer) = 0.99

The following code uses the initial guesses for  $\tau_L$  and  $SSA_L$  and the parameters listed above, calculates the variables on the right-hand sides for equations C-1a and C-1b, and is looped (using newly derived  $\tau_L$  and  $SSA_L$  values) to solve the two equations (C-1a\* and C-1b\*) for two unknowns ( $\tau_L$  and  $SSA_L$ ). Note that the calculations are broken into simple steps.

START LOOP

$$T_L = \text{EXP}(-\tau_L)$$

$$\text{const1} = (1.0 - \text{ABS}(1.0 - 2.0 * g) / 8.0 - 7.0 / 8.0 * (1.0 - 2.0 * g) * (1.0 - 2.0 * g))$$

$$\text{beta\_L} = 0.5 * (1.0 - g - 4.0 / 25.0 * \text{const1})$$

$$\text{betastar\_L} = 0.5 * (1.0 - g / 4.0 * (3.0 + \text{POW}(g, 3.0 + 2.0 * g * g * g)))$$

$$a1 = 2.0 * (1.0 - SSA_L * (1.0 - \text{betastar\_L}))$$

$$b1 = 2.0 * SSA_L * \text{betastar\_L}$$

$$c = SSA_L * \text{beta\_L}$$

$$d = SSA_L * (1.0 - \text{beta\_L})$$

$$p1 = c - a1 * c - b1 * d$$

$$p2 = -a1 * d - b1 * c - d$$

$$B = a1 * a1 - b1 * b1$$

$$\text{const1} = c - p1 / (1.0 + \text{SQRT}(B))$$

$$\text{const2} = (c - p1 / (1.0 - \text{SQRT}(B))) * \text{POW}(T_L, 2.0 * \text{SQRT}(B))$$

$$\text{const3} = 2.0 * p1 * \text{SQRT}(B) / (1.0 - B) * \text{POW}(T_L, 1.0 + \text{SQRT}(B))$$

$$\text{const4} = \text{SQRT}(B) + a1 + (\text{SQRT}(B) - a1) * \text{POW}(T_L, 2.0 * \text{SQRT}(B))$$

$$B_L = (\text{const1} - \text{const2} - \text{const3}) / (\text{const4})$$

$$\text{const1} = d + B_L * b1 + p2 / ( 1.0 + \text{SQRT}(B) )$$

$$\text{const2} = d + B_L * b1 + p2 / ( 1.0 - \text{SQRT}(B) )$$

$$\text{const3} = p2 / ( 1.0 - B ) * T_L$$

$$F_L = 1.0 / 2.0 / \text{SQRT}(B) * ( \text{const1} * \text{POW}(T_L, -\text{SQRT}(B) ) - \text{const2} * \text{POW}(T_L, \text{SQRT}(B) ) ) + \text{const3}$$

$$\text{const1} = 1.0 - \text{POW}(T_L, 2.0 * \text{SQRT}(B) )$$

$$\text{const2} = \text{SQRT}(B) + a1 + ( \text{SQRT}(B) - a1 ) * \text{POW}(T_L, 2.0 * \text{SQRT}(B) )$$

$$B^*_L = b1 * \text{const1} / \text{const2}$$

$$\text{const1} = \text{SQRT}(B) - a1 + B^*_L * b1$$

$$\text{const2} = \text{SQRT}(B) + a1 - B^*_L * b1$$

$$P^*_L = 1.0 / 2.0 / \text{SQRT}(B) * ( \text{const1} * \text{POW}(T_L, -\text{SQRT}(B) ) + \text{const2} * \text{POW}(T_L, \text{SQRT}(B) ) )$$

Find Roots solving for new  $\tau_L$  and  $SSA_L$ :

$$0 = (T_L + F_L) / ( 1.0 - B^*_L * B_M ) - P_F / P^{(0)}_F$$

$$0 = P^*_L * ( T_L + F_L ) / ( 1.0 - B^*_L * B_M ) + B_L / B_M - B_F / B^{(0)}_F$$

END LOOP

## 5.0 SOFTWARE IMPLEMENTATION

The output from the LabView code consists of a raw and processed data files. The raw data file includes the 1-Hz RS-232 output string from the instrument firmware plus the associated software-calculated values of MBC ( $\mu\text{g}$ ) and CBC ( $\mu\text{g}/\text{m}^3$ ) as described above with the sample flow and instrument status. The processed data file provides the time-weighted average CBC for the period between the user-selected start and stop times. In this case, however, the CBC is determined by a simple linear regression of the total MBC values. The CBC is then divided by the total flow measured during the sampling period. When multiple filter changes are made between the user-selected start and stop times, the software calculates an average CBC from the individual CBC values obtained for each period between the filter changes. Also shown in the processed data file are the mean

flow, flow standard deviation (SD), root mean square error of the CBC and correlation coefficient ( $R^2$ ) for each linear regression performed.

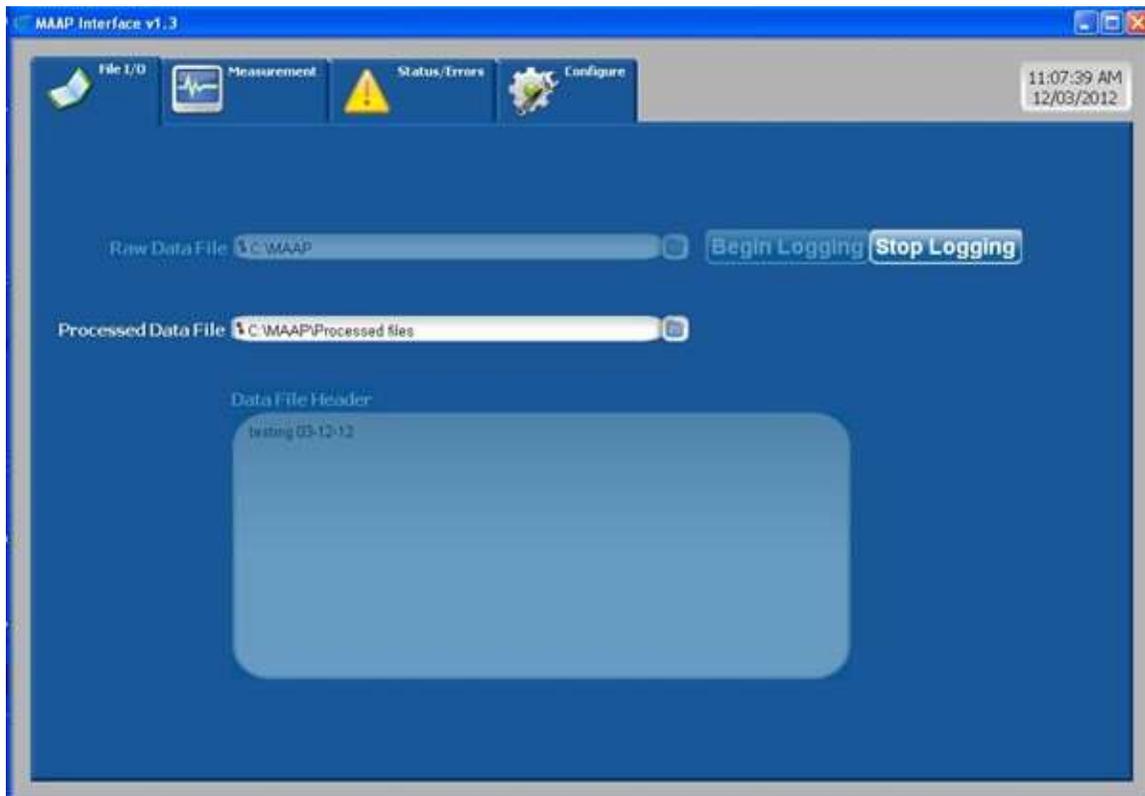
As discussed in Section 4.5 of the main text, the CBC values initially determined by the SuperMAAP during the testing program proved to be approximately 35 % lower than the other instruments evaluated. Due to this difference in the measured results, a reevaluation of the SuperMAAP and its operating software was conducted in an attempt to determine the basis for the observed differences.

Two basic problems were found that were not evident before the study began. First, the tape head was determined to contain a substantial leak whereby laboratory air was introduced into the flow downstream of the filter tape. Based on a recalibration of the entire flow system, it was determined that approximately 15 % less air was actually passing through the filter tape than was actually measured by the downstream MFC. Further experiments with different filter mass loadings showed that this leak was consistent across all operating conditions and could easily be compensated for in the MFC calibration. In addition, the existing data set could also be corrected by a simple calculation. It is generally known that the standard 5012 MAAP is not leak tight, but this leak was thought to be minimal, which was found not to be the case.

Another problem that was found involved the linear regression of the MBC values used to determine the average CBC in the LabView software. The original code calculated the linear regression over the entire sampling period by simply ignoring the time period(s) when filter changes occurred. This method created approximately a 9 % difference in the average CBC from that determined by the ARI method. Therefore, the software code was revised to calculate individual linear regressions, statistics, and average CBC for each period between filter changes and then calculate an overall average CBC and statistics from these values. This revision now provides results that are within  $1 \text{ ng/m}^3$  of the results determined by the ARI IgorPro code. In addition, a LabView post-processor was developed whereby the existing experimental data can be corrected for this problem and reported accordingly.

Also as part of the software upgrade (Version 1.3), an additional feature was added to allow the operator to view the CBC values from the 1-Hz data in real time to determine stable operating periods for analysis. New code was added to display a 5-s rolling average CBC continuously in the main window of the measurement screen in addition to the total MBC. This change allows the operator to be better informed of source operation and makes the instrument more useful. Figures C-10 through C-13 show the four output screens from the Version 1.3 LabView code.

The first screen is the file input/output screen (Figure C-10). Here the operator assigns the storage location for the raw and processed data files, starts the data-logging process, and enters any desired notations. Also displayed are the date and time from the personal computer running the LabView software. The computer time is used in the calculation of the CBC.



**Figure C-10. Updated SuperMAAP file input/output screen.**

Next the flow and MBC data are displayed in real time on the main measurement screen (Figure C-11). Also displayed on this screen are the “Start Condition” button, which starts the sampling time period; the “Stop and Calc” button, which ends sampling and calculates the average CBC value for the period; the results from the latest sampling period; the sample temperature and pressure measured by the 5012 MAAP; the total and MAAP air flow from the two external MFCs; and the filter life gauge showing the percent transmission through the filter tape. Note that the “Total Flow” is that which enters the instrument from the sampling line, and the “MAAP Flow” is the flow through the filter tape on which the average CBC is based. Also shown in the main display is the 5-s rolling average CBC.



Figure C-11. Updated SuperMAAP measurement screen (note yellow status light is on).

As indicated by its title, the status/errors screen (Figure C-12) displays the instrument operating status, warning status, and error messages produced by the 5012 MAAP firmware. The instrument is working properly if the three fields on this screen are blank. The software describes any warnings or errors displayed in these fields and also illuminates the status and/or error warning light on the main measurement screen (see Figure C-11) to alert the operator.

The last screen of the LabView software is the configure screen (Figure C-13). In this screen, the operator may enter a total flow from 0 to 20 L/min and a MAAP flow from 0 to 5 L/min to operate the SuperMAAP. Also included on this screen are fields for entering the slope and intercept of the MFC calibrations, which are then used to determine the actual total and MAAP flows for display and use in the calculations.

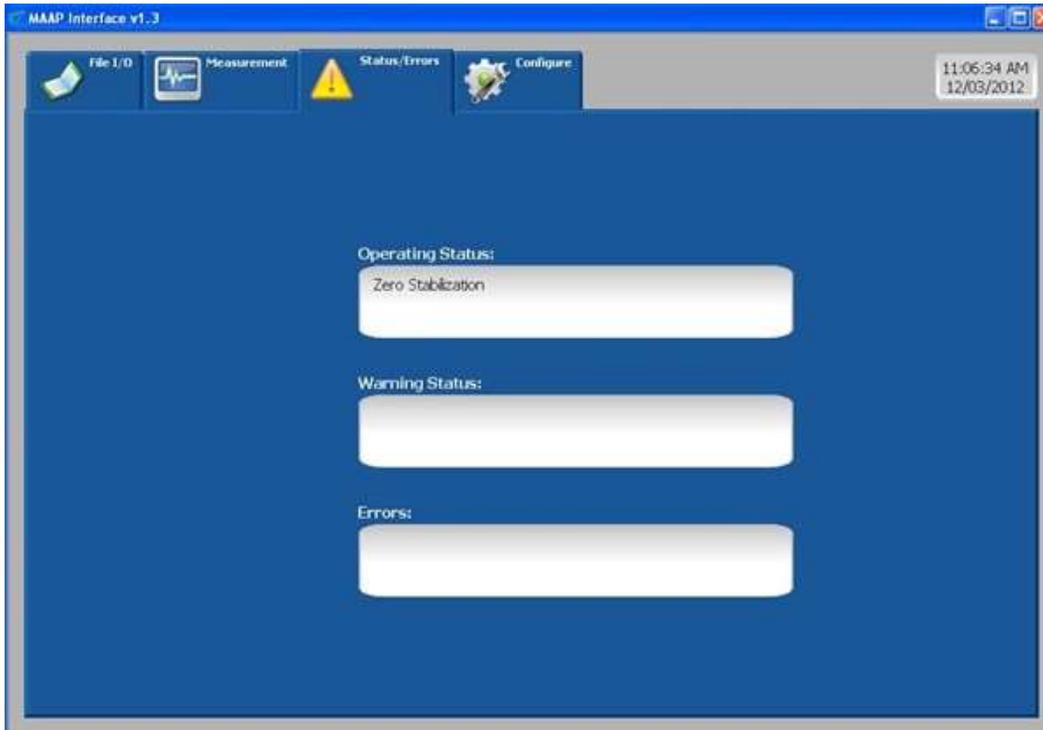


Figure C-12. Updated SuperMAAP status/errors screen (note operating status indication).

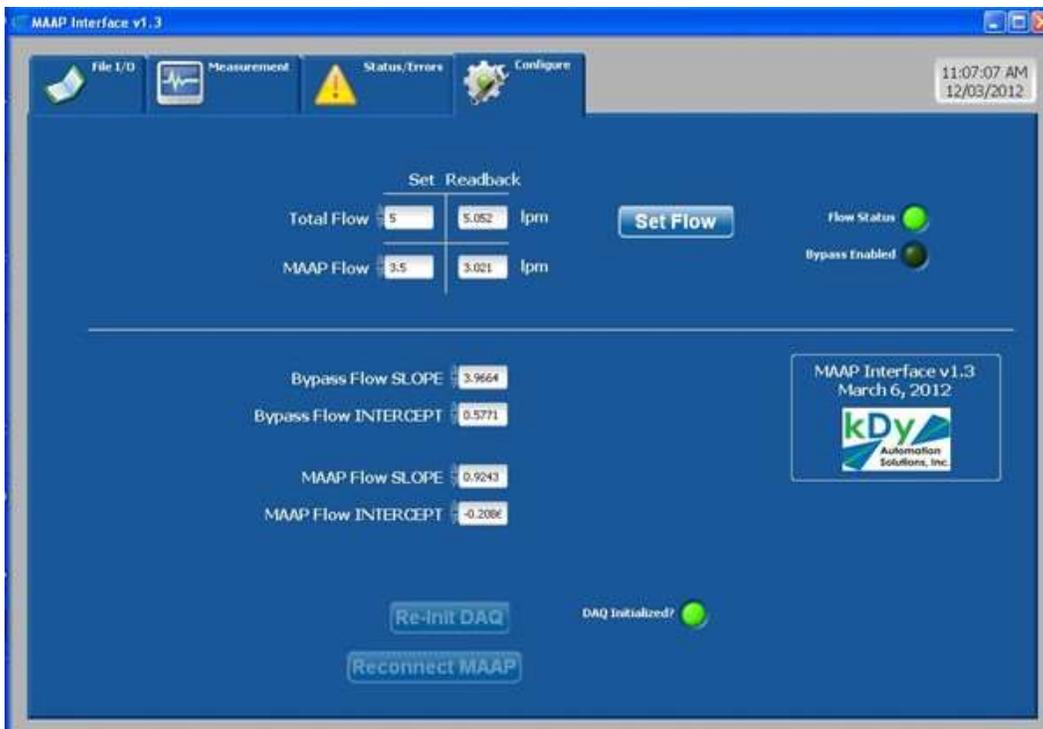


Figure C-13. Updated SuperMAAP configure screen.

## 6.0 FILTER CHANGE CORRECTION

After the study was essentially completed, the SuperMAAP was being used in another project where it was connected to a sample distribution system along with several other instruments. During sampling, it was discovered that the plumbing and operating scheme of the instrument did not isolate it from the other instruments during a filter change as originally intended. Instead, when the three-way valve was activated and the tape head opened, the software stopped the flow through the instrument, allowing laboratory air to enter the system through the optical sensor head and causing a pressure fluctuation and extra dilution for the other instruments that could not be tolerated. (Note that the MAAP modifications were made exactly as agreed upon during the workshop of experts held before the start of the study!) Therefore, a data correction method was needed. To develop this method, a detailed flow characterization and tracer gas study was performed.

As the first step, a flow characterization was conducted of the entire sampling system and instrumentation shown in Figure C-3. In this study, the backflow created during a SuperMAAP filter change was determined using a DryCal flow meter located at the sample inlet as well as various other points throughout the instrument flow system. During these measurements, it was determined that only approximately 40 cm<sup>3</sup>/min of laboratory air was introduced into the sampling system during a filter change. Since it is doubtful whether this small amount of dilution air would substantially affect the measurements made by the other instruments, a tracer gas experiment was designed to quantitatively assess the measurements made by the other instruments during a SuperMAAP filter change.

To conduct the tracer gas measurements, compressed N<sub>2</sub> gas containing 8720 ppm CO<sub>2</sub> was introduced at 4.9 L/min into the bottom of the cyclone (Figure C-3) upstream of the instruments with the sampling tunnel blower operating at 23 Hz (equivalent to the 100 µg/m<sup>3</sup> target concentration when the MiniCAST burner was used). The CO<sub>2</sub> concentration was then measured sequentially at each sampler or instrument location using a calibrated Horiba Model VA-3000 infrared gas analyzer to obtain the diluted CO<sub>2</sub> concentration at each point. These concentrations were measured before, during, and after at least two filter changes at each location in the system to determine differences in CO<sub>2</sub> concentration. Using the data obtained, the difference in the measured concentration was determined and compared with the other instruments in the system, and a data correction scheme was developed from the data. Table C-2 shows the data collected during the tracer gas experiment.

**Table C-2. Results of SuperMAAP Tracer Gas Study**

<b>Segments</b>	<b>Average CO<sub>2</sub> (ppm)</b>	<b>Sample Duration</b>	<b>Duration of Filter Change</b>
Teflon filter sample	796 ± 0		
SuperMAAP filter change #1	821 ± 7	0:01:58	0:01:31
Teflon filter sample	799 ± 0		
SuperMAAP filter change #2	822 ± 6	0:02:12	0:01:43
Teflon filter ambient	382 ± 1		
Quartz filter sample	791 ± 0		
SuperMAAP filter change #1	799 ± 4	0:02:28	0:01:44
Quartz filter sample	791 ± 0		
SuperMAAP filter change #2	799 ± 4	0:02:12	0:01:39
Quartz filter ambient	384 ± 1		
MSS sample	794 ± 1		
SuperMAAP filter change #1	813 ± 8	0:02:04	0:01:30
MSS sample	793 ± 0		
SuperMAAP filter change #2	812 ± 6	0:02:18	0:01:43
MSS ambient	380 ± 0		
LII sample	796 ± 0		
SuperMAAP filter change #1	812 ± 5	0:02:05	0:01:34
LII sample	794 ± 0		
SuperMAAP filter change #2	810 ± 4	0:02:06	0:01:40
LII ambient	379 ± 0		

As shown in Table C-2, there was approximately a 3 % higher CO<sub>2</sub> concentration observed during the SuperMAAP filter change as compared to before and after the change. However, the higher concentration lasted only approximately 2 min, a factor that must be considered within the overall test period that could be as long as 7 h. Another factor that must be considered is the number of filter changes occurring over the test period. Therefore, using the data in Table C-2, a data correction template was developed that mathematically determines the total time when the SuperMAAP is undergoing a filter change (change in duration × number of changes per test) and the percent decrease in concentration measured by each instrument during that period. These values were then used to adjust the test averaged PM concentration measured by the two filter samplers, LII, and MSS considering the overall duration of the test period. The corrected values obtained using this template are reported in Section 5 of the main document.

## 7.0 REFERENCES

Petzold, A.; Schönlinner, M. (2004). Multi-angle absorption photometry—a new method for the measurement of aerosol light absorption and atmospheric black carbon. *Journal of Aerosol Science*, 35, 421–441.

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Petzold, A.; Schloesser, H.; Sheridan, P. J.; Arnott, W. P.; Ogren, J. A.; Virkkula, A. (2005). Evaluation of multiangle absorption photometry for measuring aerosol light absorption. *Aerosol Science and Technology*, 39, 40–51.

# Appendix D: Measurement of Nonvolatile Particulate Matter Mass Using the Modified Multi-angle Absorption Photometer (MAAP)— Thermo Fisher Scientific

STANDARD OPERATING PROCEDURE 2106

NRMRL/APPCD

APPROVED: September 6, 2011



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## 1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) provides instructions for the measurement of nonvolatile particulate matter (nvPM) mass using the modified Model 5012 multi-angle absorption photometer (MAAP) manufactured by Thermo Fisher Scientific (Waltham, MA, USA).

The Model 5012 MAAP measures black carbon (BC) in ambient air. The off-the-shelf instrument has been specially modified by the Air Pollution Prevention and Control Division (APPCD) to allow its use for source measurements through the addition of externally mounted hardware and customized LabView software (National Instruments, Austin, TX, USA). Thus, this modified instrument can be used to quantify the emissions of nvPM at the exit plane of aircraft gas turbine engines. The measurement value of the MAAP is concentration of BC ( $\mu\text{g}/\text{m}^3$ ).

This SOP outlines a step-by-step procedure that describes how to set up and run the instrument as well as to retrieve the data during operation of the modified Model 5012 MAAP.

## 2.0 METHOD SUMMARY

The Model 5012 MAAP measures ambient and source BC concentrations and aerosol light absorption properties. The instrument is based on the principle of aerosol-related light absorption and the corresponding BC mass concentration. The MAAP analyzes the modification of radiation fields caused by deposited particles in the front and back hemispheres of a glass-fiber filter. The data inversion algorithm is based on a radiation transfer method and therefore takes into account multiple scattering processes inside the deposited aerosol and between the aerosol layer and the filter matrix. The reduction of light transmission, multiple reflection intensities, and air sample volume are continuously integrated over the sample run period to provide real-time data output of BC concentration measurements.

## 3.0 DEFINITIONS

**Nonvolatile PM:** Particle emissions that exist at gas turbine engine exit plane temperature and pressure conditions and that do not contain volatile particle contributions that condense at lower temperatures.

**Soot:** Carbonaceous particles that are by-products of the combustion of liquid or gaseous fuels.

#### **4.0 MAAP MODEL 5012 MODIFICATIONS**

The following modifications were made by APPCD to the off-the-shelf MAAP instrument:

- Capability for reduced air flow through the filter tape to extend its useful life.
- Automated isolation of the MAAP from the main sampling line during the filter changes.
- Incorporation of calculations to determine BC concentrations on a 1-Hz basis and logging of the data.
- Calculation of the average BC concentration at the end of the run.
- Capability to force a manual filter change at any time during the run.
- Ability to monitor the transmission percentage in real time so that the operator can determine when a filter change is about to take place.
- Fabrication of an add-on equipment “package” that incorporates the necessary changes for use in engine certification environments.

#### **5.0 EQUIPMENT AND SUPPLIES**

- Modified Model 5012 MAAP.
- Additional hardware (parts list) used to make the “box-on-the-box” (see Figure D-1) that will be provided as separate documentation.
- Two main power cables (one for the MAAP and a second for the “box-on-the-box”).
- RS-232 communication cable.
- External vacuum pump connected to the MAAP.
- LabView software – Version 1.

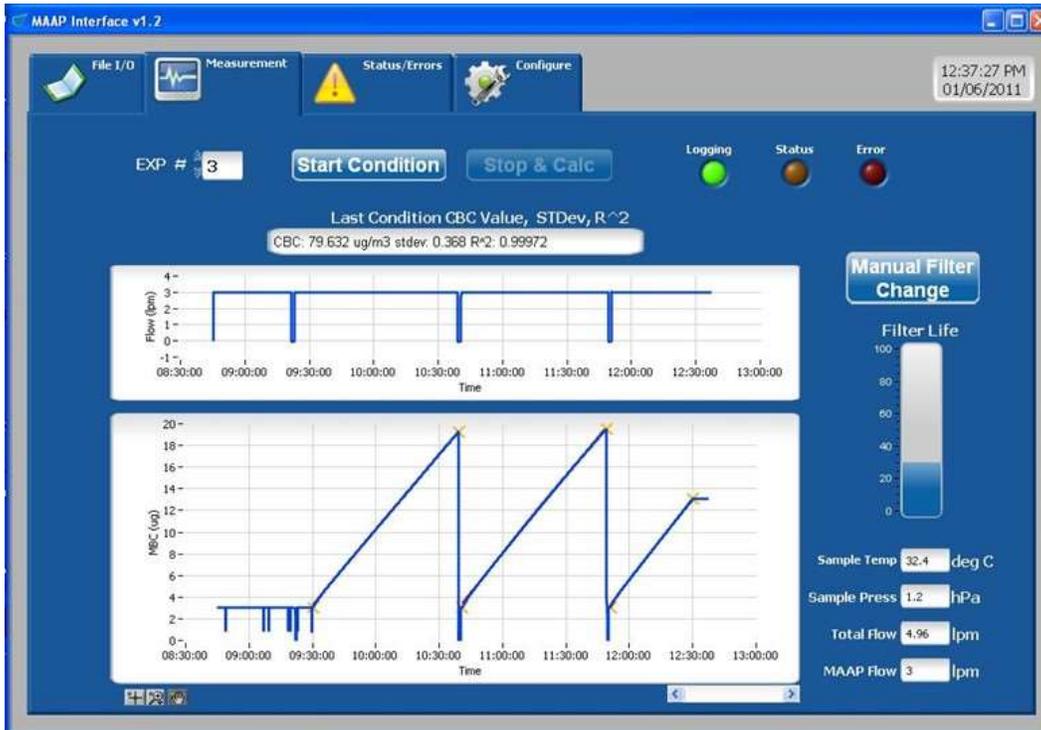


Figure D-1. Modified MAAP Model 5012 showing the “box-on-the-box.”

## 6.0 PROCEDURES

### 6.1 Sample Collection and Instrument Operation

1. Turn on both the MAAP and the external vacuum pump.
2. Start the computer with the MAAP software.
3. In the LabView software, go to the MEASUREMENT screen (Figure D-2) and click on MANUAL FILTER CHANGE to force this manual operation. The status light will turn on and the pump will go off during this step.



**Figure D-2. MAAP software – Measurement view.**

4. Also enter the experiment number (EXP #) in the MEASUREMENT screen.
5. Go to the CONFIGURE screen (Figure D-3) and enter the TOTAL FLOW and MAAP FLOW. These flows are regulated by mass flow controllers installed in the “box-on-the-box” and calibrated by the APPCD Metrology Laboratory according to MOP FV-0237.0 (U.S. EPA, 2010) within 1 year of use.
6. Go to the FILE I/O screen (Figure D-4) and choose locations for both raw and processed data files. Press BEGIN LOGGING, which starts data logging for the raw data file. The raw data file contains all output data from the MAAP plus the values calculated from those data. Not all raw data are used in the calculations for the processed data file.
7. Go again to MEASUREMENT view and press START CONDITION. These data are now used to calculate the concentration of BC (CBC) shown in the processed data file.

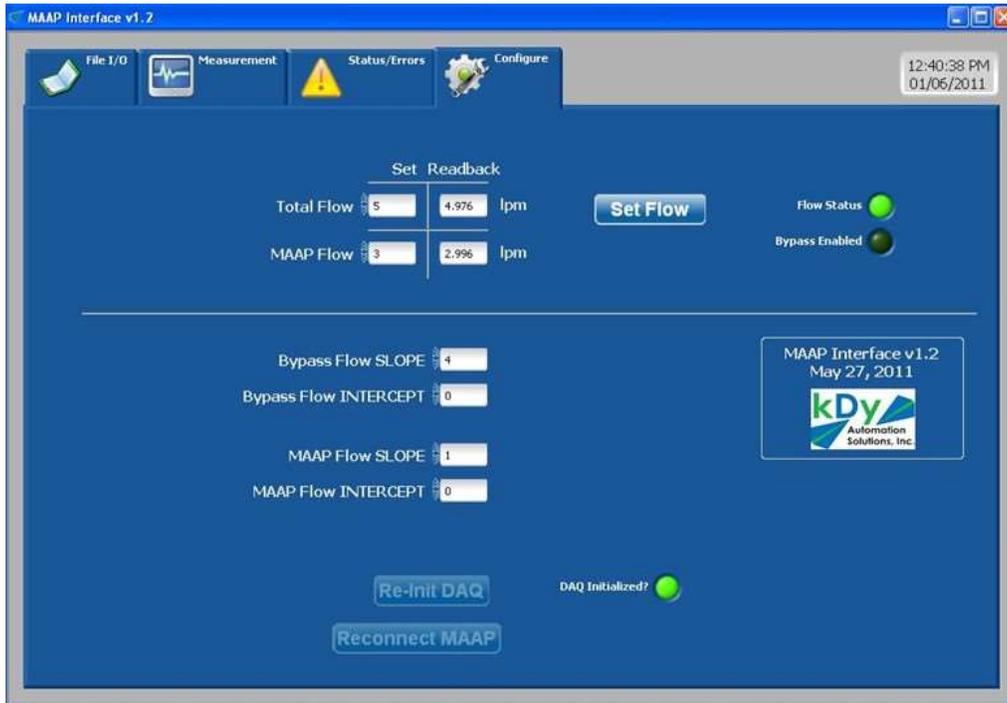


Figure D-3. MAAP software – Configure view.

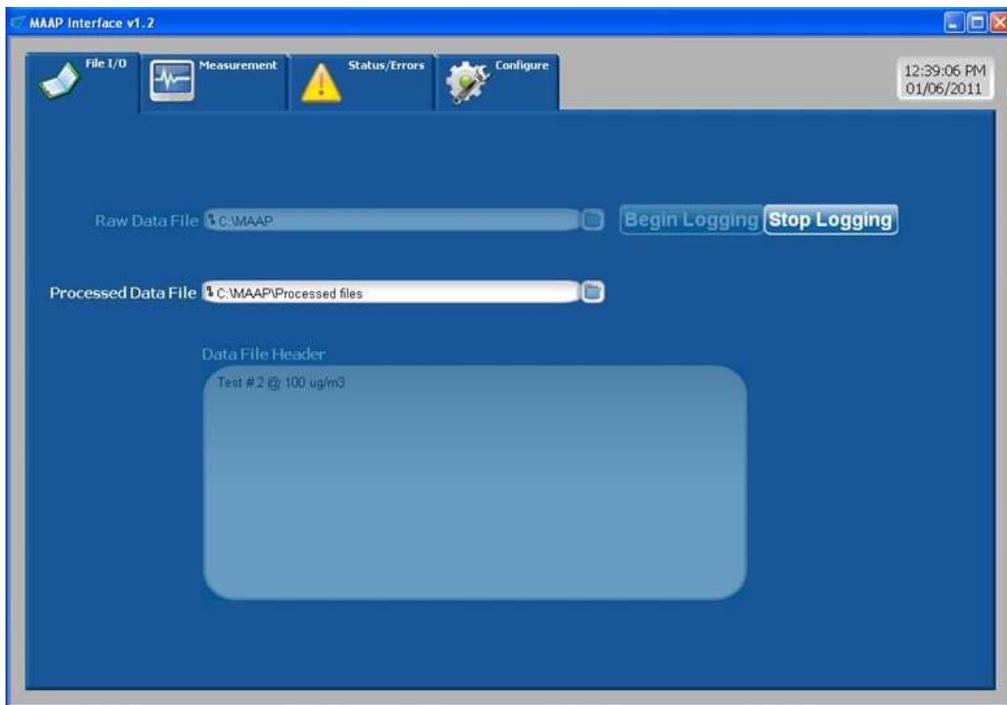


Figure D-4. MAAP software – File I/O view.

NOTE: In the middle of the measurement, the Filter Change operation can occur if the transmission is lower than 20 %, but the filter change will not influence the calculated results. This operation is handled in the LabView software program.

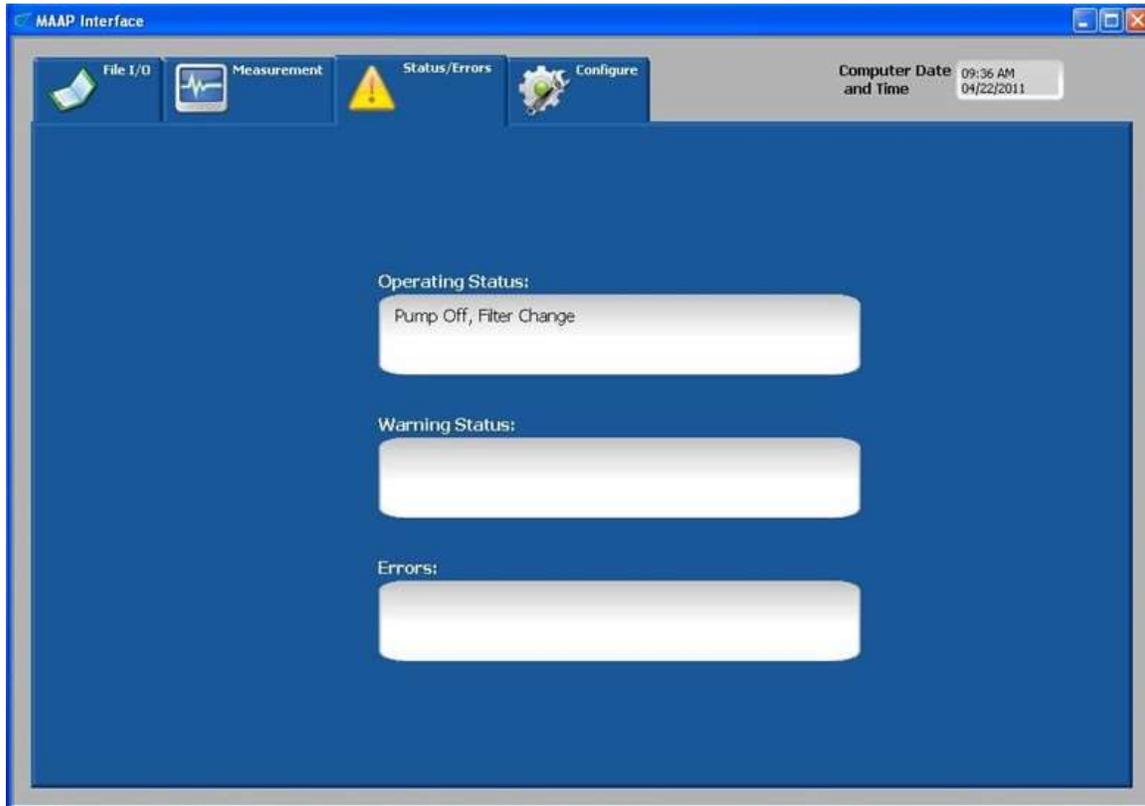
8. After the desired sampling time, press STOP and SAVE in the MEASUREMENT view and STOP LOGGING in the FILE I/O view in order to stop all data logging. The processed data file is automatically produced and average values calculated by the software using a linear regression of the mass of BC on the filter tape divided by the average air flow rate.
9. Before starting a new measurement cycle, make sure that the Filter Change operation is performed.

## **6.2 Data Acquisition, Calculations, and Data Reduction**

- 6.2.1 The format for the processed data file is shown in an attachment (Section 10.1). The processed data file contains the following information: Start and Stop Time (h:min:s), Exp #, number of points used for calculation, mean flow rate (L/min) and standard deviation (SD), CBC ( $\mu\text{g}/\text{m}^3$ ), and CBC root-mean-square error (RMSE) and  $R^2$  for the linear regression of the mass of BC calculated by the software.
- 6.2.2 The software application automatically produces and stores both the raw and processed data files.
- 6.2.3 The BC average mass concentrations are generated directly in the processed data file and expressed as “Black Carbon Concentration CBC ( $\mu\text{g}/\text{m}^3$ ).” No additional calculation is necessary.

## **6.3 Troubleshooting**

- 6.3.1 In general, three different types of status messages are possible: operating, warning, and error (Figure D-5). These messages are not controlled and cannot be addressed with the new MAAP computer software. They are created from the MAAP instrument itself.
- 6.3.2 One of the most common and expected status messages is shown in Figure D-5 and is caused by a manual or automatic filter change.
- 6.3.3 Explanation of status messages and correction of errors are described in the original MAAP Model 5012 instruction manual (Thermo Fisher Scientific, 2003 or later).



**Figure D-5. MAAP software – Status/Errors view.**

## **7.0 FUNCTIONALITY TEST**

The functionality test of the MAAP refers to the emission power of the light-emitting diode (LED) and to the signal level of the photodetectors. This test is conducted as follows:

1. Force a manual filter change and then turn off the pump.
2. Go to the SERVICE menu and read the photosensor bit values. The values of the photodetectors must be in the following ranges:
  - Transmission and two reflection diodes between 3000 and 3900.
  - Reference diode between 1500 and 3900.

If the values are in this range, the instrument is functioning properly. Otherwise, contact the instrument manufacturer. For further details, refer to Chapters 2 and 3 of the Thermo Operating Manual for more specific instructions on setting up the instrument and

operating parameters. This test should be conducted prior to each set of measurements for QC purposes.

## **8.0 DATA AND RECORDS MANAGEMENT**

**8.1** Individual electronic data files are generated for each sample run. All data files are stored appropriately in the data acquisition system. At the end of each day's testing, all files generated are archived and identified appropriately.

**8.2** Laboratory notebooks are used to document the following:

- Test conditions and times.
- Sampling system parameters.
- Samples collected.
- Background soot concentrations before and after the measuring cycle.
- Any unusual events or difficulties.

**8.3** All hand-recorded data (laboratory notebooks and data sheets) must be written accurately and legibly, and all errors and discrepancies must be noted.

## **9.0 REFERENCES**

Thermo Fisher Scientific. (2003 or later). Model 5012 Multi Angle Absorption Photometer (MAAP) Instruction Manual, P/N 100076-00. Thermo Scientific Corporation, Franklin, MA.

U.S. Environmental Protection Agency (U.S. EPA). (2010). Procedure for Calibration of a Mass Flow Controller (MFC) Using a Gilibrator<sup>®</sup>, MOP FV-0237.0. National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, Research Triangle Park, NC.

## 10.0 ATTACHMENTS

### 10.1 Processed Data File Format

TEST-G @100 µg/m <sup>3</sup>								
Start Time	Stop Time	Exp #	# Points	Mean Flow	Flow SD	CBC	CBC Fit RMSE	CBC Fit R <sup>2</sup>
				L/min		µg/m <sup>3</sup>		
12:22:02	13:24:12	2.1	2855	2.997	0.006	85.343	0.405	1
13:25:52	14:20:11	2.2	2454	2.997	0.006	95.179	0.488	1
14:21:53	15:02:40	2.3	1828	2.997	0.006	92.295	0.565	1
15:04:32	15:22:01	2.4	784	2.996	0.006	96.154	0.844	0.999
12:22:02	15:22:01	2 (avg)	7921	2.997	0.006	91.065	0.511	1

# Appendix E: Measurement of Nonvolatile Particulate Matter Mass Using the LII 300 Laser-Induced Incandescence Instrument

STANDARD OPERATING PROCEDURE 2102

NRMRL/APPCD

APPROVED: August 6, 2012



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## 1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) provides instructions on the measurement of nonvolatile particulate matter (nvPM) mass concentration using the LII 300 laser-induced incandescence instrument from Artium Technologies, Inc. (Sunnyvale, CA, USA).

The LII 300 instrument measures black carbon (BC) soot from air pollution sources. This method can therefore be used to quantify the emissions of nvPM at the exit plane of aircraft gas turbine engines. The parameter measured by the LII 300 is mass concentration of soot ( $\text{mg}/\text{m}^3$ ).

This SOP is a step-by-step procedure that describes how to set up and run the instrument as well as to retrieve the data during operation of the LII 300 instrument.

## 2.0 METHOD SUMMARY

The LII 300 is an instrument for non-intrusive and real-time measurements of soot particulate concentration and primary particle size. With this technique, a pulsed laser is used to rapidly heat the soot particles within the measurement volume from the local ambient temperature to close to the soot vaporization temperature ( $> 4000 \text{ K}$ ). Soot particle incandescence is detected by two detectors using appropriate line filters, and the signals are recorded for subsequent analysis.

The LII 300 is completely insensitive to liquid particles because they absorb a negligible amount of laser energy compared to carbon. For carbon particles coated with volatile material, the volatiles are believed to vaporize early in the laser heating period. For calibration of the LII, a novel method (self-calibrating) was developed based on absolute light intensity measurement that avoids the problem of calibration with a known source of soot particles. That method applies two-color pyrometry principles to determine the particle temperatures, relating the measured signals to the absolute sensitivity of the system as determined with a strip filament lamp.

## 3.0 DEFINITIONS

**Nonvolatile PM:** Particle emissions that exist at gas turbine engine exit plane temperature and pressure conditions and that do not contain volatile particle contributions that condense at lower temperatures.

**Soot:** Carbonaceous particles that are by-products of the combustion of liquid or gaseous fuels.

## **4.0 HEALTH AND SAFETY CONSIDERATIONS**

- 4.1** This device must not be used in any environment where there is a danger of explosion. Ignitable or explosive exhaust gas mixtures or exhaust gases that are ignitable or explosive when mixed with air must not be measured with the device.
- 4.2** Some components can get very hot during operation. If necessary, use heat-resistant protective gloves.
- 4.3** Exhaust gas of combustion engines contains toxic substances. If used in a test cell, ensure appropriate ventilation and proper discharge of the exhaust, which must meet current industry standards. Make sure to check the leak-tightness of the probe connectors on both the sampling point and the device.
- 4.4** The device contains a Class 4 semiconductor laser that is embedded and protected by suitable measures so that the device has been classified as a Class 1 laser product. Every service of the laser must be carried out only by service staff trained in laser safety measures.

## **5.0 EQUIPMENT AND SUPPLIES**

### **5.1 Instrumentation**

- Self-contained LII 300.
- Laser power supply.
- Hand-held controller for the laser power supply.
- External pump capable of supplying flow of approximately 5 L/min.
- Rotameter capable of measuring flow of approximately 5 L/min.

### **5.2 Ancillary Equipment and Supplies**

- Two main cables for 110 V AC.
- Input/output (I/O) cable to connect the LII 300 unit with the laser power supply.
- Two cooling water hoses: blue and red.
- 9-Pin RS-232 cable to connect the LII 300 unit with the laser power supply.
- Polypropylene tubing (1/4-in. OD) to connect an air supply (50 to 250 psi) to LII 300 unit.
- BNC connector to connect the LII 300 unit to the laser power supply.

- AIMS software for instrument remote control.
- Wireless router for interconnection of LII 300 unit with the PC.
- Power key switch for laser power supply unit.
- Distilled water (approximately 710 mL).
- Air supply (“shop air”) of at least 50 psi (max 250 psi).
- Operational check lamp provided by Artium Technologies, Inc.

### 5.3 Installation

Refer to Figure E-1 for illustration of steps 2 through 10.

1. Connect the laser I/O cable from the laser power supply (#1) to the LII 300 unit (#1 and #2).
2. Connect the blue and red cooling water tubes from the laser power supply unit (#4 and #5) to the LII 300 unit (#3 and #4).
3. Connect a power cord to the laser power supply (#3) unit and LII 300 unit (#14).
4. Follow steps 4a through 4g to fill the laser cooling reservoir properly with distilled water:
  - a. Connect the fill bottle to the FILL/DRAIN fitting located on the front side of the laser power supply unit.
  - b. Connect the fitting with hose to the upper VENT fitting.
  - c. Add distilled water to the bottle until the water drains from the vent fitting.
  - d. Disconnect both coolant fittings.
  - e. Turn the key switch ON and the pump will turn on automatically after power-up.
  - f. When the reservoir empties, turn the key switch OFF and repeat steps 4a through 4d.
  - g. Add distilled water to the reservoir until the “maximum level” is maintained in the coolant level window, with the pump running.
5. Connect a 9-pin RS-232 cable from the laser power supply unit (#2) to the RS-232 connector on the back of the LII 300 unit (#11).
6. Connect an air supply (50 to 250 psi) to the CLEAN DRY AIR connection on the LII 300 unit (#7).

7. Connect the BNC connector from the laser power supply unit Q-Switch Sync (#6) to the LII 300 unit (#12).
8. Connect the printer cable from the LII 300 unit (#9) to the wireless router.
9. Connect the external pump (with rotameter) to SAMPLE OUT (#6) on the LII 300 unit.
10. Connect the sample line to SAMPLE IN (#5) position on the LII 300 unit.
11. No.13 on the LII 300 unit is the optional external heater connection. If not used, leave cap installed.
12. No. 8 on the LII 300 unit is the spare USB and # 10 spare serial connections.
13. No. 7 on the laser power supply unit is the optional interlock switch. If not used, leave the BNC cap installed.
14. Connect the hand-held controller to the front of the laser power supply (Figure E-2). Make sure that the red emergency shutoff button is in the out position.

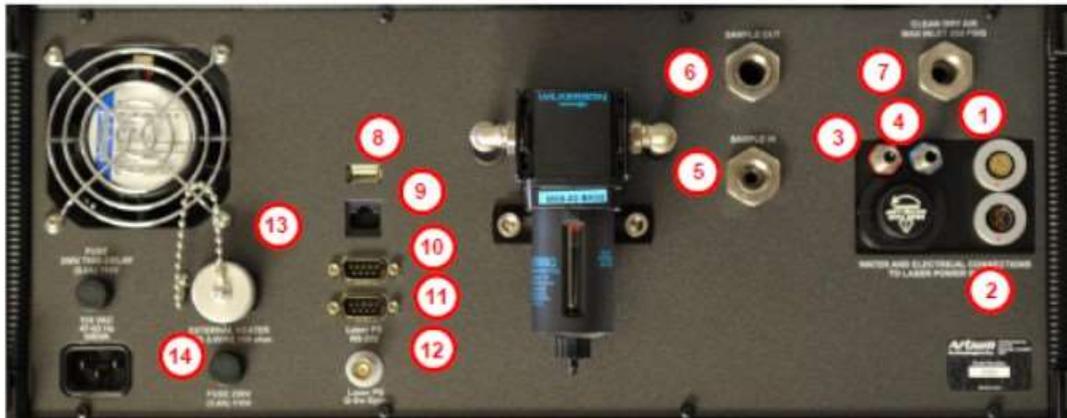
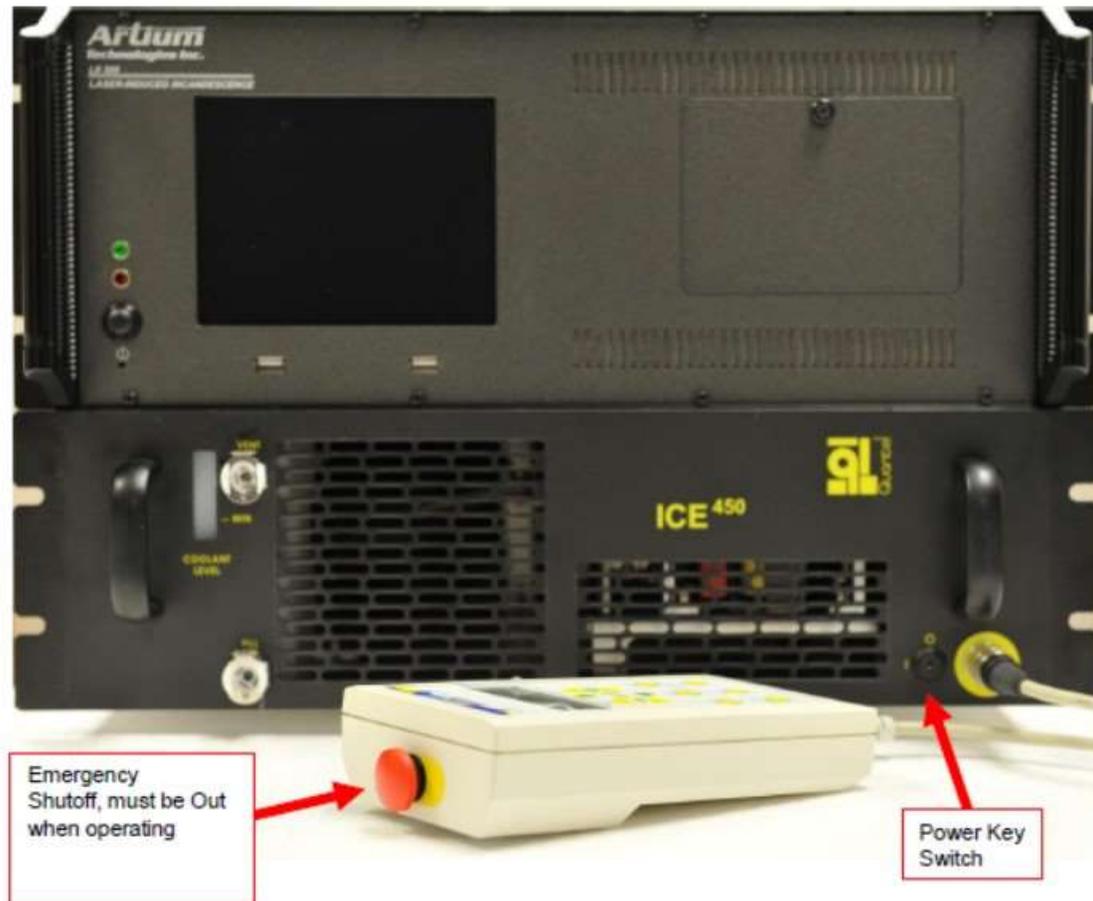


Figure E-1. Back side of LII 300 unit (top photo) and laser power supply (two bottom photos) with marked connections.



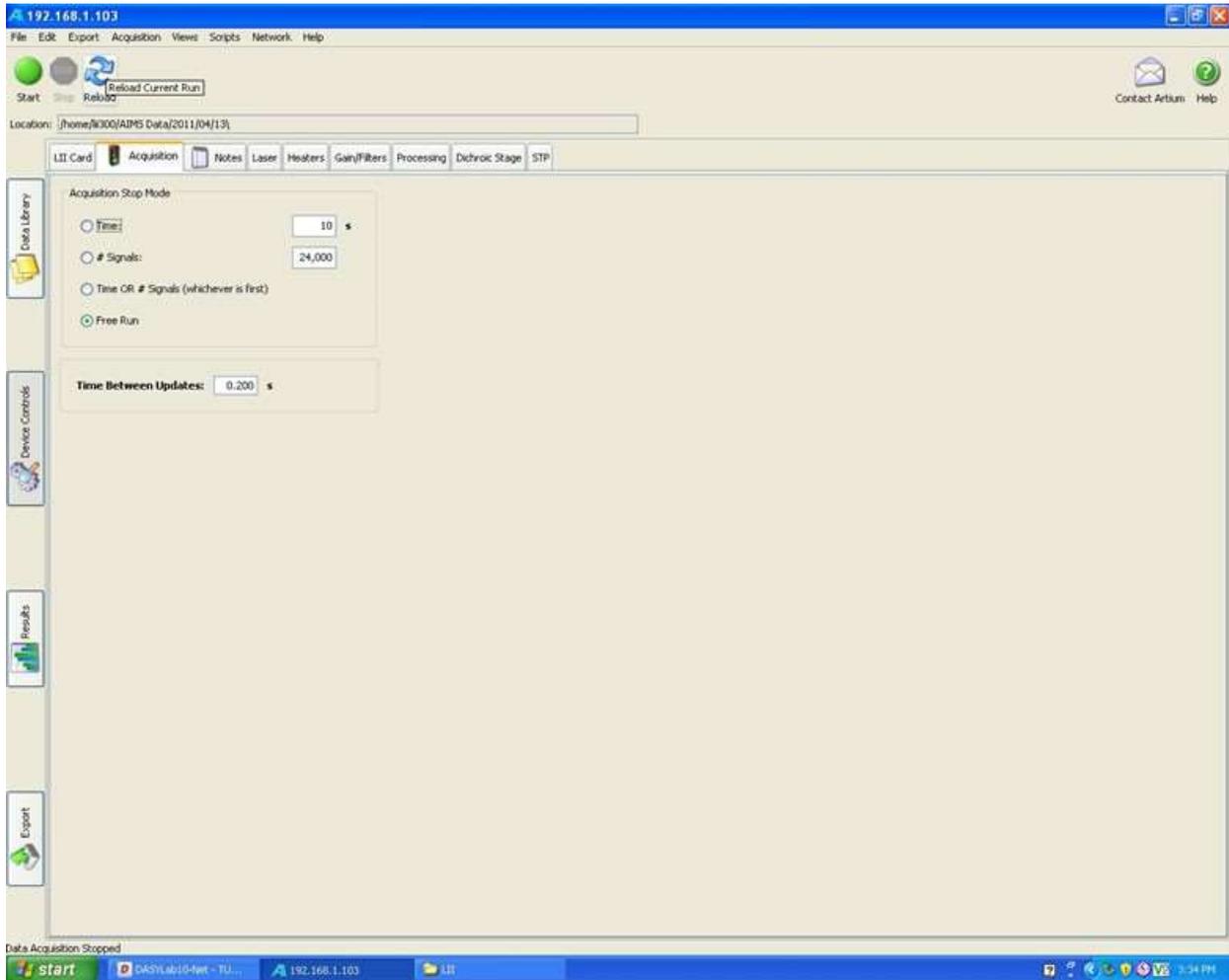
**Figure E-2. LII 300 optics enclosure, laser power supply, and hand-held controller front panel.**

## 6.0 PROCEDURES

### 6.1 Sample Collection and Instrument Operation

1. Use the key on the front panel (Figure E-2) to turn on the laser power supply unit (clockwise).
2. Turn on the LII 300 unit by using the power button on the front panel. The red power light-emitting diode (LED) will come on and remain on.
3. Connect and start the computer with the AIMS software.
4. To set up an external pump on the LII 300 front panel touch screen, choose “SETTINGS” → “SAMPLE CELL” → “SAMPLE VALVE”.

5. Check “Disable ejector vacuum pump” and press the “Open Valve” button.
6. Plug in the pump and check the flow on the rotameter (should be ~ 5 L/min).
7. To control and review device parameters, click on the DEVICE CONTROL icon (Figure E-3) located on the left side of the window.
8. The user must check the following parameters:
  - a. Under ACQUISITION, select FREE RUN (as shown in Figure E-3).
  - b. Under GAIN/FILTERS, select AUTOMATIC GAIN and AUTOMATIC FILTER.
  - c. Under STP, enter standard temperature and pressure (STP) all final results will be calculated using that set of STP conditions.
9. All other options in all other tabs should remain unchanged.
10. Click on the start acquisition button () to start data acquisition.
11. Click on the stop acquisition button () to stop data acquisition.



**Figure E-3. Device control – online view.**

## **6.2 Data Acquisition, Calculations, and Data Reduction**

- 6.2.1** Clicking the DATA LIBRARY icon (Figure E-3) located on the left side of the window opens folders that contain the results files.
- 6.2.2** Double clicking any of the files opens them in graphic form under the RESULTS icon, also located on the left side of the window.
- 6.2.3** Clicking on the EXPORT icon (left side of window) exports the run file to the format selected under EXPORT → PREFERENCES.

- 6.2.4 Data format depends on the configuration of the export template. The sample data form with selected mass concentration and primary particle size (PPS) versus time can be found in Attachment 9.1.
- 6.2.5 The software application automatically stores data acquired during an analysis in individual electronic data files for later computation, display, and printing.
- 6.2.6 The BC mass concentrations are generated directly and expressed as concentration of soot in exhaust ( $\text{mg}/\text{m}^3$ ) at 25 °C and 1013 mbar (760 mm Hg).

### 6.3 Troubleshooting

- 6.3.1 The AIMS software displays alerts and recommendations in the Status Window (Figure E-4).
- 6.3.2 The Status Window pops up automatically when an alert or error is received, but it can also be found by pressing F7 or selecting Help → Show Status Window.

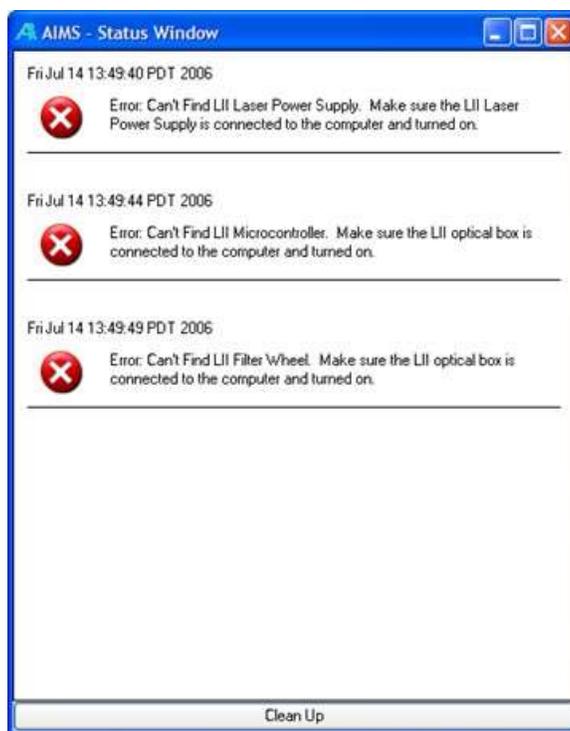


Figure 4. Status window – online view.

## 6.4 Draining Water from the LII 300 and Laser Power Supply

**6.4.1** The water from both devices must be drained before shipping the units:

1. Disconnect the quick-disconnect coolant lines from the LII 300 unit (Figure E-1). Tilt the unit to allow the coolant to drain into a catch basin.
2. Blow dry nitrogen gas through the left (blue) coolant connector on the LII 300 to remove any remaining coolant. Install the shipping cover over the output of the laser head and the blue coolant port plugs. The LII 300 is now ready for long-term storage or shipping.

**6.4.2** To drain the plumbing in the laser power supply (Figure E-1), attach the connectors provided with the accessories kit to both cooling lines. Place the blue-colored hose into a catch basin and turn the power supply key switch to ON. Allow the pump to run only as long as coolant continues to flow into the catch basin.



**CAUTION:** Do not run the pump motor dry for an extended period of time as this will cause permanent damage.

When looking at the front of the cabinet, the drain and fill fittings are located on the left side of the cabinet.

1. Place the water bottle (~ 2 L) below the lower drain fitting of the laser power supply to catch the waste coolant.
2. Install the white plastic quick-disconnects supplied with the accessories kit into the fill/drain and vent fittings on the front of the cabinet. Water should flow out of the lower drain fitting. Be sure to keep the drain bottle below the level of the power supply unit.
3. With the blue coolant line in the catch basin, blow dry nitrogen into the red-colored coolant line until no more water exits the power supply unit. Next, with the red line in a catch basin, blow dry nitrogen into the blue-colored coolant line until no more water exits the unit.
4. To drain the coolant lines, detach the coolant hoses from the back of the power supply unit. Hold the end of the coolant hoses (with coolant change connectors installed in the stainless steel connectors) over a catch basin. Press the white plastic part that protrudes from the end of the plastic connectors. When depressing this part, do not cover the

entire end of this connector as it will not allow the coolant to drain from the lines.

5. Again install the white plastic quick-disconnects supplied with the accessories kit into the drain and fill fittings on the front of the cabinet. Water should flow out of the lower drain fitting. Any residual coolant left in the cooling system after following this procedure is not a concern. Disconnect the white fittings from the front of the panel. The coolant is now drained and the power supply unit is suitable for storage or transport.

## **7.0 DATA AND RECORDS MANAGEMENT**

**7.1** Individual electronic data files are generated for each sample run. All data files are stored appropriately in the data acquisition system. At the end of each day's testing, all files generated are archived and identified appropriately.

**7.2** Laboratory notebooks are used to document the following:

- Test conditions and times.
- Sampling system parameters.
- Samples collected.
- Background soot concentration before and after the measuring cycle.
- Any unusual events or difficulties.

**7.3** All hand-recorded data (laboratory notebooks and data sheets) must be written accurately and legibly, and all errors and discrepancies must be noted.

## **8.0 QUALITY CONTROL AND QUALITY ASSURANCE**

### **8.1 Quality Control Procedures**

The operational check lamp (Figure E-5) is used to check the general operation of the instrument and to detect any system failures. Before using the check lamp, the sample cell heater needs to be set to room temperature. To set the sample cell heater, go to SETTINGS mode on the LII 300 front panel, and then choose SAMPLE CELL → HEATERS → SAMPLING CELL HEATER.

The SAMPLING CELL HEATER option allows the user to change the temperature of the sampling cell. The set point should be approximately 20 °C. Cooling of the sample cell can take up to 30 min or longer.



**Figure E-5. Operational check lamp.**

1. Once the sample cell has returned to room temperature, open the sample cell access door located on the front panel of the LII 300 unit.
2. Remove the screw from the test cell circled in red and shown on Figure E-6.
3. Plug the USB cable end of the operational check lamp into the USB port on the front panel of the LII 300 unit while inserting the calibration LED into the test cell.
4. Use the locking screw to tighten the check lamp into place as shown in Figure E-7.
5. Then go to SETTINGS mode on the LII 300 front panel, and choose OPTICS → OPERATIONAL CHECK.
6. Press the UPDATE button to force the LII 300 to acquire approximately 3 seconds of data and average the signal levels.
7. Compare “Current” to “Factory” values. Deviation between values should be < 10 % (if higher contact the manufacturer).



**Figure E-6. Front panel of the LII 300 showing the sample cell access door.**



**Figure E-7. Front panel of the LII 300 unit showing the operational check lamp.**

## 8.2 Quality Assurance Procedures

### 8.2.1 *Sample Cell Temperature Calibration*

The temperature calibration allows the user to calibrate the temperature sensors on the sample cell. To perform the calibrations, go to SETTINGS → SAMPLE CELL → TEMPERATURE CALIBRATION. Press the UPDATE button to force the LII 300 to perform the action. The calibration is set to the default offset of 0 and a scale of 1; in this case, the raw value should equal the corrected value:

$$\text{temperature}_{\text{corrected}} = (\text{temperature}_{\text{raw}} \times \text{scale}) + \text{offset}$$

### 8.2.2 Sample Cell Pressure Calibration

The pressure calibration allows the user to calibrate the pressure sensors on the sample cell. Since the pressure sensor measures pressure relative to the atmospheric pressure, there is a field in the pressure calibration to input the local/current atmospheric pressure. To perform the calibrations, go to SETTINGS → SAMPLE CELL → PRESSURE CALIBRATION. Press the UPDATE button to initiate the action. An example of the calibrated pressure is shown in Figure E-8. The calibration is set to the default offset of 0 and a scale of 1; in this case, the raw value should equal the corrected value:

$$\text{pressure}_{\text{corrected}} = (\text{pressure}_{\text{raw}} \times \text{scale}) + \text{offset.}$$

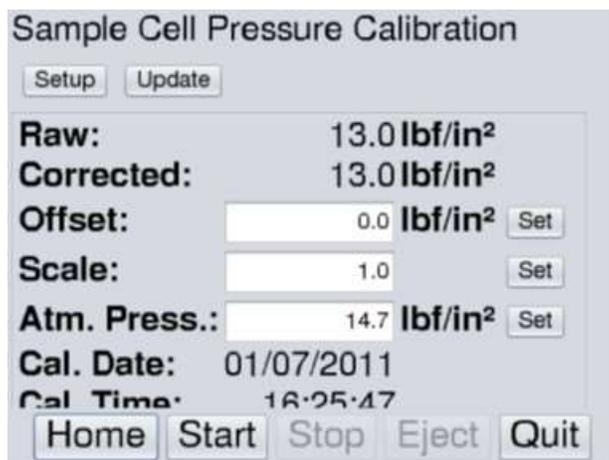
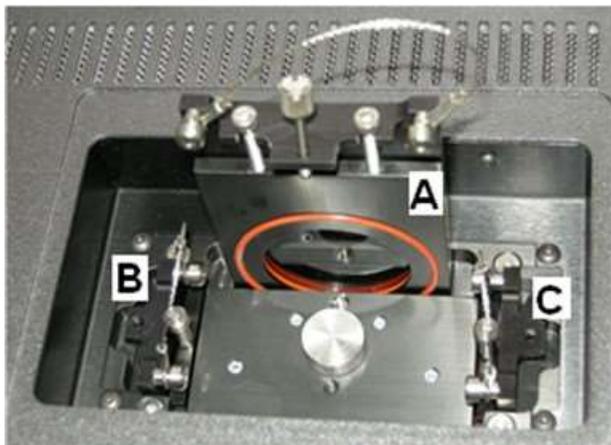


Figure E-8. Pressure calibration screen.

### 8.3 Regular Maintenance

Since the LII instrument bases measurements on absolute intensity measurements of the soot incandescence, window contamination can systematically bias the results. The windows need to be examined occasionally for contamination. The

LII 300 unit has three windows: one large horizontal window (Figure E-9A) and two side vertical windows (Figure E-9B and C).



**Figure E-9. Extracting the horizontal sample cell window for cleaning.**

The following steps describe how to access and clean the windows:

1. Loosen the thumb screw holding the sample cell door on the front panel of the LII 300 and remove the door. A safety switch will deactivate the laser when the door is removed.
2. Unscrew the lockdown thumbscrew on the window frame as shown in Figure E-9.
3. Grasp the cable and pull out firmly on the window frame and retaining device.
4. Note the proper orientation of the windows in the frame.
5. Remove the window and frame from the the retaining device and clean the window. A clean cloth may be used, and if there is condensed material on the window, a solvent may be used. Use a clean cloth to finish cleaning.
6. Replace the window in the frame and reinsert the frame.
7. Lock down the window with the thumbscrew.
8. Place the sample cell doors in their starting position.

## 9.0 ATTACHMENTS

### 9.1 Sample Data Form

Time (ms)      Mass Concentration (mg/m<sup>3</sup>)      PPS (nm)

12:01:20:288	0.681	39.6
12:01:21:289	0.212	24.5
12:01:22:288	0.111	55.9
12:01:23:288	0.08	15.5
12:01:24:288	0.158	5.5
12:01:25:288	0.09	12
12:01:26:288	0.065	15
12:01:27:288	0.169	4.1
12:01:28:288	0.242	9.1
12:01:29:288	0.262	10.6
12:01:30:288	1.555	14.7
12:01:31:288	0.978	49.3
12:01:32:288	0.67	24.5
12:01:33:288	2.336	19.1
12:01:34:288		
12:01:35:288	2.222	32
12:01:36:288	0.964	9.9
12:01:37:287	0.545	13.3
12:01:39:288	0.819	8.5
12:01:40:288	2.432	125.8
12:01:41:287	3.649	38.6
12:01:42:287	4.414	134.9
12:01:43:287	2.396	50.6
12:01:44:287	2.025	28.8
12:01:45:287	3.221	20
12:01:46:287	2.582	28.2
12:01:47:287	0.926	9.2
12:01:48:287	1.447	10.3
12:01:49:287	0.228	10.7
12:01:50:287	0.047	27.9

# Appendix F: Measurement of Nonvolatile Particulate Matter Mass Using the AVL 483 Micro Soot Sensor Photoacoustic Analyzer with AVL Exhaust Conditioning Unit

STANDARD OPERATING PROCEDURE 2105

NRMRL/APPCD

APPROVED: August 2, 2012



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## 1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) provides instructions on the measurement of nonvolatile particulate matter (nvPM) mass concentration using the AVL 483 Micro Soot Sensor (MSS) photoacoustic analyzer with AVL exhaust conditioning unit (AVL List GmbH; Graz, Austria).

The AVL 483 MSS measures black carbon (BC) soot, which is emitted from air pollutant sources. Thus, this method can be used to quantify the emission of nvPM at the exit plane of aircraft gas turbine engines. The measured value of the AVL 483 MSS is concentration of soot in exhaust ( $\text{mg}/\text{m}^3$ ).

This SOP is a step-by-step procedure that describes how to set up and run the instrument as well as to retrieve the data during operation of the AVL 483 MSS.

## 2.0 METHOD SUMMARY

The AVL 483 MSS is based on the photoacoustic effect. With this measurement method, an intensity modulated “chopped” light beam produces periodic heating (when “on”) of absorbing particles, which dissipate their heat in the “off” state. A microphone detects the resulting pressure fluctuations. Clean air produces a zero signal, avoiding the drawback of the light extinction method. The microphone signal is linearly related to the BC concentration in the measuring volume. A more complete description of the photoacoustic method is provided in various references such as Schindler et al. (2004).

## 3.0 DEFINITIONS

**Measuring device:** AVL 483 Micro Soot Sensor (MSS).

**Conditioning unit:** AVL exhaust conditioning unit.

**Nonvolatile PM (nvPM):** Particulate matter (PM) emissions that exist at gas turbine engine exit plane temperature and pressure conditions and that do not contain volatile particle contributions that condense at lower temperatures.

**Soot:** Carbonaceous particles that are a by-product of the combustion of liquid or gaseous fuels.

**Operating stages:**

**Sleep:** Power-up stage. All running functions are switched off.

**Pause:** Warm-up and checking stage. The temperature controls of the measuring cell and the thermoelectric cooler are switched on. The window pollution, flow (pump switched on for a short while), and resonance frequency are checked.

**Standby:** The pump is started. The window pollution and the resonance frequency are checked again. The average “zero value” is also determined.

**Measurement:** The analyzed exhaust gas is directed to the measuring cell. The logging of the measurement data is started.

**Zero check:** Clean, filtered air (“zero gas”) is directed to the measuring cell and the measurement values are used for the baseline correction.

#### 4.0 HEALTH AND SAFETY CONSIDERATIONS

- 4.1 This device must not be used in any environment where there is a danger of explosion. Ignitable or explosive exhaust gas mixtures or exhaust gases that are ignitable or explosive when mixed with air must not be measured with the device.
- 4.2 Some components can get very hot during operation, especially if they are located near the tailpipe. If necessary, use heat-resistant protective gloves.
- 4.3 Exhaust gas of combustion engines contains toxic substances. If used in a test cell, ensure appropriate ventilation and a proper discharge of the exhaust. Make sure to check the leak-tightness of the probe connectors on both the sampling point and the device.
- 4.4 The device contains a Class 4 semiconductor laser with invisible radiation of 808-nm wavelength and a power of up to 2 W. The laser is embedded and protected by suitable measures so that the device has been classified as a Class 1 laser product.
- 4.5 All service must be carried out only by service staff trained in laser safety measures:
  - Switch off the measuring device before opening the measuring chamber.
  - If one of the LEDs in the measuring chamber is illuminated after the cover has been opened, the device must be switched off immediately.
  - Removal of the cooler unit at the back of the measuring chamber is strictly forbidden.

## 5.0 LIMITS OF APPLICATION

- 5.1** The suction power of the pump is set with a throttling valve so that approximately 3.8 L/min are pulled at the inlet of the pump unit at a negative pressure of 300 mbar. In the measuring unit, the sample flow is split into a *by-pass flow* and a *measuring flow* that passes through the measuring cell. Both flows should be approximately equal and between 1.8 and 2 L/min.
- 5.2** The photoacoustic measuring principle limits the pressure in the measuring chamber and therefore also the pressure at the input of the measuring device to the ambient pressure of  $\pm 50$  mbar. The conditioning unit ensures that the inlet pressure of the measuring chamber is within that specification and up to a maximum pressure of 2 bar (rel.).
- 5.3** The temperature of the exhaust gas at the input of the measuring device must not exceed 60 °C. The conditioning unit can condition exhaust gas temperatures of 1000 °C (less than 60 s) and 600 °C (in continuous operation).
- 5.4** The exhaust gas must not contain any condensate droplets and no condensation water may form in the entire system. The conditioning unit can be used to dilute the exhaust gas (dilution ranges from 2 to 20) to prevent it from condensing.
- 5.5** The maximum soot concentration that can be measured is 50 mg/m<sup>3</sup> with 1 µg/m<sup>3</sup> sensitivity and a minimum detection limit of 5 µg/m<sup>3</sup>.
- 5.6** Information about the technical data for the measuring device, conditioning unit, and pressure-reducing unit can be found in Attachment 11.1.

## 6.0 EQUIPMENT AND SUPPLIES

### 6.1 Instrumentation

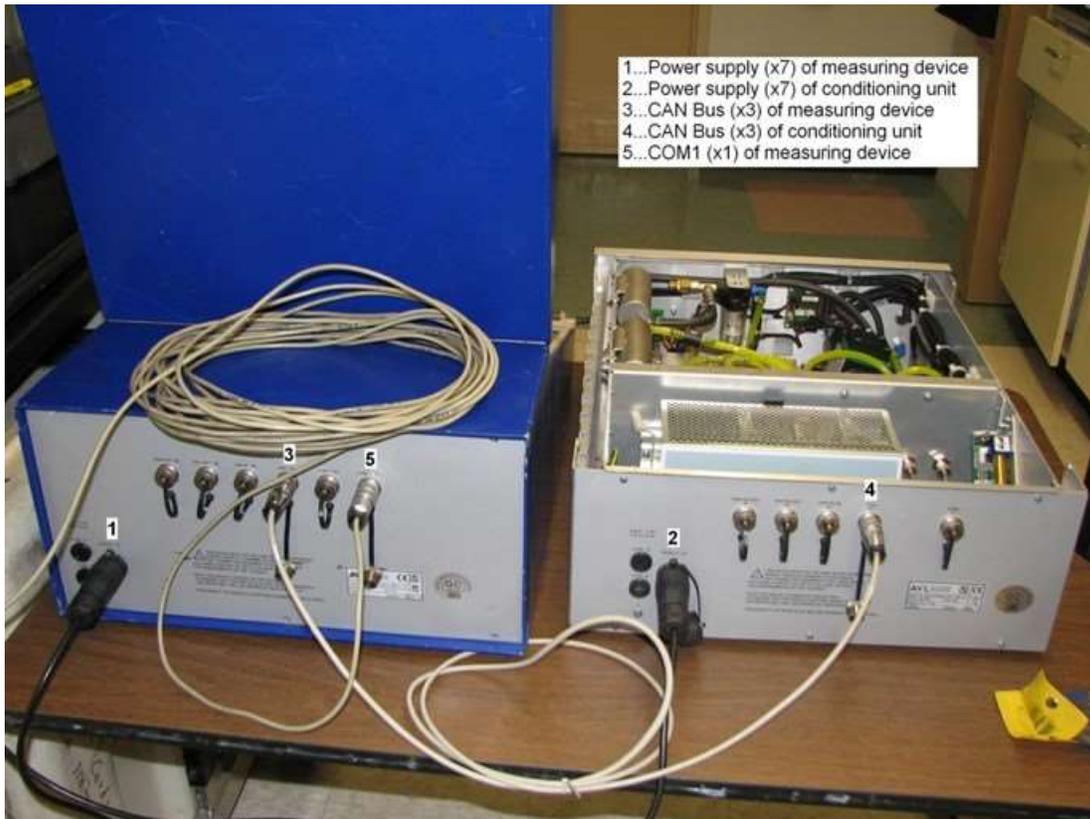
- AVL 483 Micro Soot Sensor (BO6529).
- AVL exhaust conditioning unit with pressure-reducing module with dilution cell (BO7354).
- A suitable sampling probe and line (provided by others).

## **6.2 Ancillary Equipment**

- Two main cables for 110 V AC (BV2166).
- CAN connecting cable measuring device – conditioning unit (BV2988).
- Connecting hose measuring device – dilution unit, 2 m (BO6533).
- Connecting hose dilution cell, 2m (SS0178).
- Connecting Viton hose measuring device – dilution cell (SS0215).
- Heating for sample line (TM0483S1HT.01).
- PC software – measuring device control software (TM048PCA.01).
- High-performance particulate filters, 10 pcs (MM0336).
- Probe filters (for pump unit), 10 pcs (MF0478).
- Serial cable for RS-232 connection (BV1854).
- Polyester cleaning cloths (HP0206).

## **6.3 Installation**

1. Refer to Figure F-1 for illustration of steps 2 through 5.
2. Connect the power cable with the socket (x7) at the back of the measuring device (1).
3. Connect the power cable with the socket (x7) at the back of the conditioning unit (2).
4. Connect the CAN bus (x3) connector of the measuring device (3) and the CAN bus (x3) connector of the conditioning unit (4) using the CAN connecting cable.
5. Connect the serial cable to the COM1 (x1) interface at the back of the measuring device (5).



**Figure F-1. Connections between measuring device and conditioning unit – back side.**

6. Connect EXHAUST IN on the conditioning unit with EXHAUST OUT on the measuring unit using the quick-connect hose (Figure F-2).
7. Connect the sample inlet tube to the EXHAUST IN pipe on the measuring device.



**Figure F-2. Connections between measuring device and conditioning unit – front side.**

## **7.0 PROCEDURES**

### **7.1 Sample Collection and Instrument Operation**

1. Connect and start the computer with the AVL software.
2. Turn on both the measuring device and the conditioning unit.
3. In the AVL software (Figure F-3), go to drop down menu SETTINGS, click on USER, and select REMOTE.
4. Click the PAUSE button. Approximately 25 min is needed to warm up. A resonance test and zero value determination will automatically be performed when the device is ready for measurement.

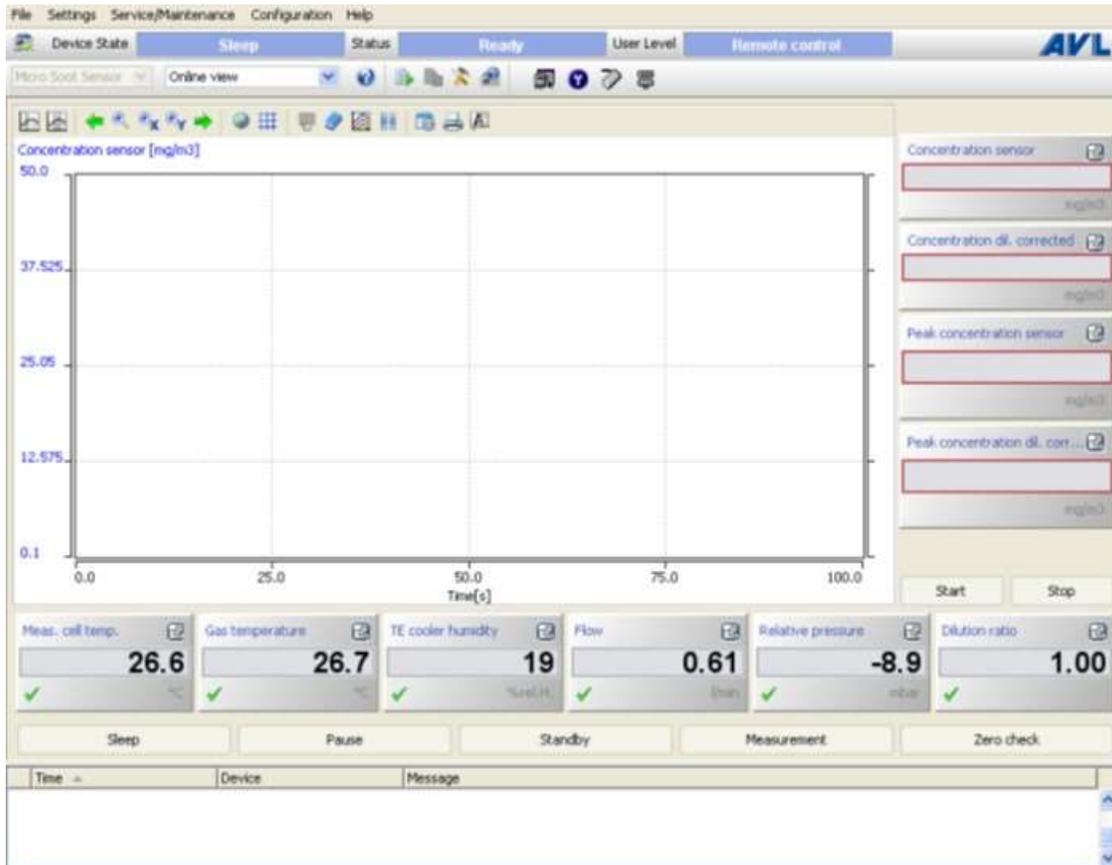
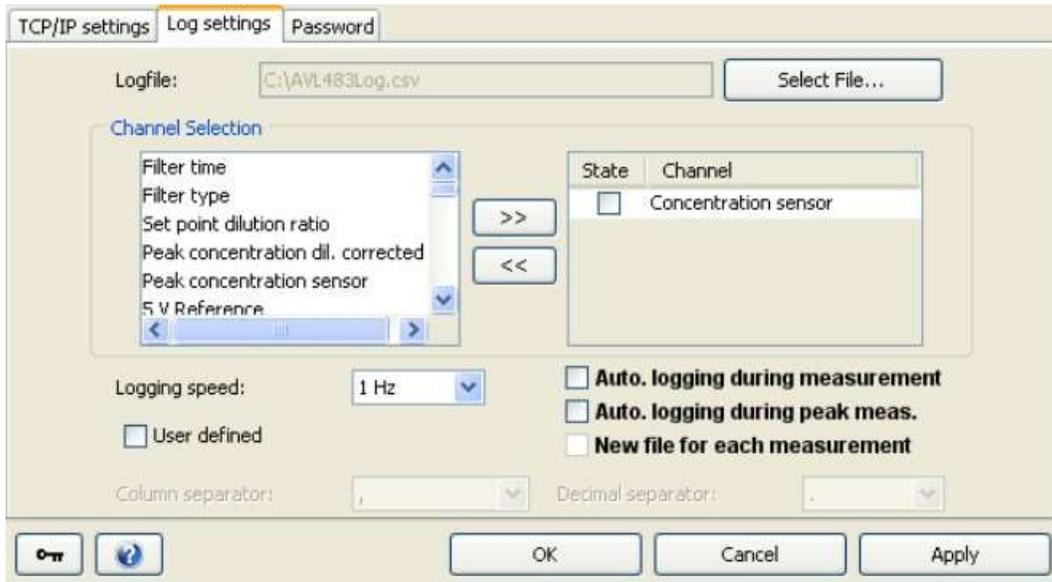


Figure F-3. AVL device control software – online view.

5. During warm-up, select FILE → DEVICE CONFIGURATION → LOG SETTINGS (Figure F-4) to input the file name, desired location, logging channels, etc:
  - a. Select the channels that need to be logged. When NO DILUTION is selected, the common channel selections should include concentration sensor, flow, absolute pressure, gas temperature, and zero signal.
  - b. Select “Auto logging during measurement.”
  - c. Select “New file for each measurement.”
  - d. Choose logging speed of 1 Hz.
  - e. Click on SELECT FILE to change the file name and location. You can select either CSV or TXT as the file type.



**Figure F-4. Log settings – online view.**

6. Once the device is warmed up, place it in STANDBY position (~ 60 s to stabilize).
7. Instead of ONLINE VIEW shown in Figure F-3, select SERVICE VIEW (NUMERICAL) and record the following values:
  - a. Zero signal (window pollution): 0.0–1.4 mV.
  - b. Resonance frequency: ~ 4100 Hz.
  - c. Max. raw meas. value: 230–30 mV.
  - d. Measuring cell temp. at test: ~ 52 °C.
8. Once the values have been recorded during STANDBY, choose SETTINGS → CONDITIONING. For 0 dilution select NO DILUTION in the menu and click APPLY. For a dilution ratio of 2–20, select CONDITIONING UNIT, set the dilution, and click APPLY.
9. Record the background soot concentration shown at the end of the STANDBY cycle.
10. Start sampling by selecting the MEASUREMENT option. Measuring cycles should not be longer than 30 to 60 min to avoid significant window pollution.
11. When the testing is finished, select ZERO CHECK and let the device run for 30–60 seconds. If the measuring value has drifted (for example, because of window pollution), the original zero value will not be reached. In this case, the

measuring value obtained in the operating state ZERO CHECK can be used for the baseline correction.

12. Select either PAUSE (for long breaks) or STANDBY (to get unit ready for next measurement) to stop logging and measuring.
13. At the end of the day, put the unit in either PAUSE or SLEEP and close the program.
14. Turn off both the measuring device and the conditioning unit.

## 7.2 Data Acquisition, Calculations, and Data Reduction

**7.2.1** Data format depends on the channel selection (Section 7.1, step 5a).

**7.2.2** The software application automatically stores data acquired during an analysis in individual electronic data files for later computation, display, and printing. A data form sample can be found in Attachment 11.2.

**7.2.3** The BC mass concentrations are generated directly and expressed as concentration of soot in exhaust ( $\text{mg}/\text{m}^3$ ) at  $0\text{ }^\circ\text{C}$  and 1013 mbar (760 mm Hg). To recalculate that value to the EPA standard temperature and pressure (STP) conditions ( $25\text{ }^\circ\text{C}$  and 760 mm Hg), the following formula must be applied:

$$C_{\text{stp}} = \frac{C}{1.092} (\text{mg}/\text{m}^3) = C \times 0.92 (\text{mg}/\text{m}^3)$$

where:

$C_{\text{stp}}$  is the soot concentration under STP conditions ( $25\text{ }^\circ\text{C}$  and 760 mm Hg).

$C$  is the soot concentration at  $0\text{ }^\circ\text{C}$  and 760 mm Hg generated by the instrument.

1.092 is the number representing the ratio of temperatures  $T_{\text{stp}}/T$  in K (298K/273K).

## **7.3 Troubleshooting**

- 7.3.1** In general, two different types of messages are possible: errors and warnings.
- 7.3.2** Messages with an error and warning code smaller than 100 refer to the measuring device, and messages with a code greater than 100 refer to the conditioning unit.
- 7.3.3** In the event of either warning or error, the red status LED on the device flashes.
- 7.3.4** Warnings inform the user that a maintenance action is required. The user should eliminate the error as soon as possible. When a warning is generated, the device firmware does not take any actions and the currently running actions are continued.
- 7.3.5** Three different types of errors are possible: operating, device, and commissioning errors. Device errors and some operating errors are detected by the firmware, and the firmware takes actions to correct them.
- 7.3.6** Error and warning codes are listed in Attachment 11.3 together with a short description and required corrective action.
- 7.3.7** For detailed explanations of each error code as well as how to recognize and correct the commission errors (firmware does not recognize them), please refer to the instrument manual.
- 7.3.8** If an error cannot be rectified by simple maintenance actions and persists, the failure must be resolved by a service technician.

## **8.0 DATA AND RECORDS MANAGEMENT**

- 8.1** Individual electronic data files are generated for each sample run. All data files are stored appropriately in the data acquisition system. At the end of each day's testing, all files generated are archived with proper identification.
- 8.2** Laboratory notebooks are used to document the following:
- Test conditions and times.
  - Sampling system parameters.

- Samples collected.
- Background soot concentration before and after the measuring cycle.
- Any unusual events or difficulties.

**8.3** All hand-recorded data (laboratory notebooks and data sheets) must be written accurately and legibly, and all errors and discrepancies must be noted.

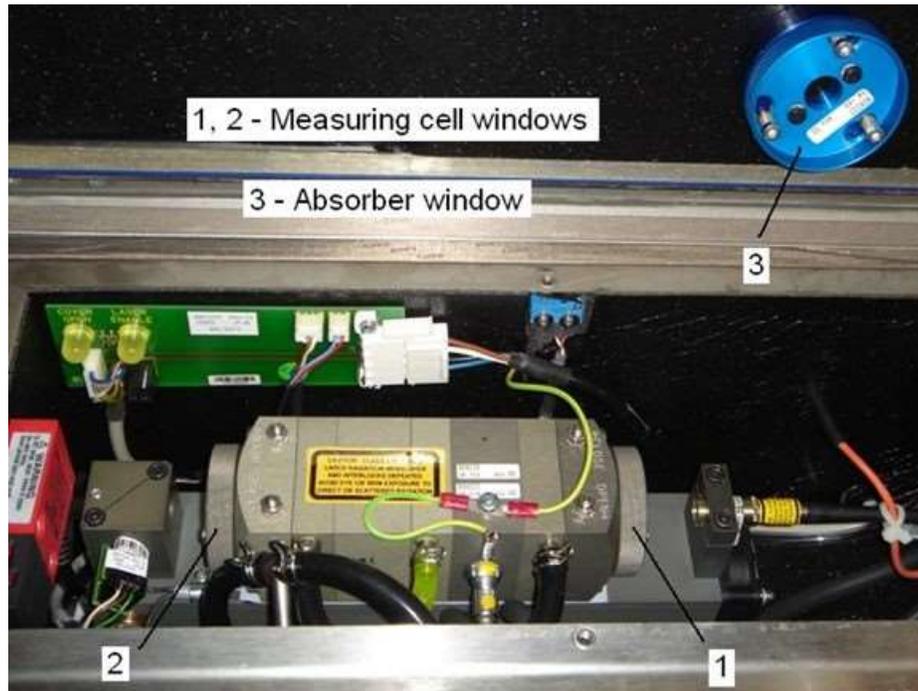
## **9.0 QUALITY CONTROL AND QUALITY ASSURANCE**

### **9.1 Quality Control Checks**

#### **9.1.1 Calibration Check**

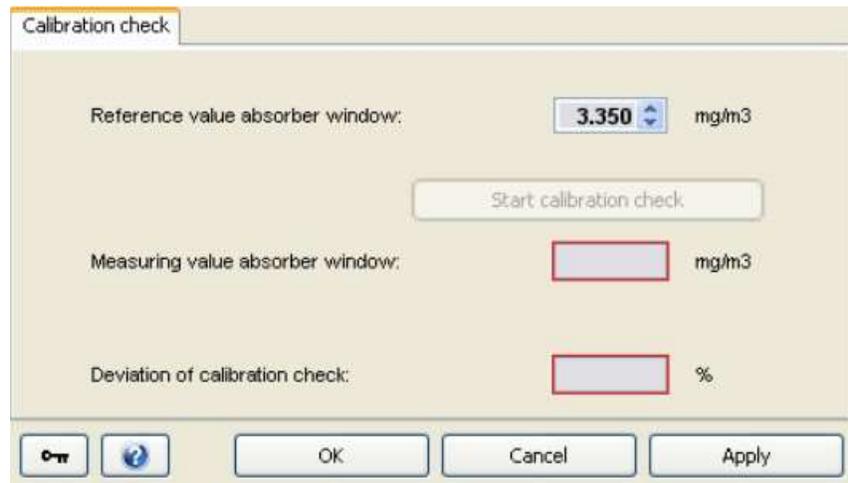
The entire sensor sensitivity (the intensity of the laser beam and the sensitivity of the microphone) is checked by means of an absorber window. The calibration check should be carried out at least once a month or once a week, depending on the instrument use.

1. The measuring device should be warmed up and in the operating state PAUSE or STANDBY
2. Change to the operating state SLEEP.
3. Switch off the measuring device.
4. Open the lid of the measuring device.
5. Remove the five screws of the measuring chamber cover.
6. Lift off the cover of the measuring device.
7. Remove the window on the right-hand side (Figure F-5 [1]) by turning the quick lock.
8. Insert the absorber window (blue calibration window on the cover of measuring device, Figure F-5 [3]) so that the writing on the series number sticker is horizontal.



**Figure F-5. Measuring cell and absorber windows (open lid view).**

9. Close the cover, refasten the five screws, and close the lid of the measuring device.
10. Switch on the measuring device and change to the operating state SLEEP.
11. In the software, select the menu item SERVICE/MAINTENANCE → CALIBRATION CHECK (Figure F-6).
12. Click on START CALIBRATION CHECK (check takes ~ 20 min).
13. The deviation of the measured value expressed as DEVIATION OF CALIBRATION CHECK should be approximately 2–3 %, not to exceed 10 %. In the event of deviations exceeding 10 %, it is recommended to return the instrument to AVL for a factory recalibration.



**Figure F-6. Calibration check – online view.**

14. After the calibration check, the device is in the operating state SLEEP. Switch off the measuring device and lift off the cover.
15. Remove the absorber window and fix it on the cover of the measuring device.
16. Fix the standard window and close the cover.
17. Retighten the five screws and close the lid.

### **9.1.1 Zero Check**

In the STANDBY operation state, the window pollution is checked automatically before each measurement by measuring the primary signal values (in mV) with clean air in the measuring cell. The window pollution is checked to determine whether these values are below 1.5 mV.

1. Zeroing should be performed again after each measurement cycle (measuring time of 30 to 60 min) by switching to the STANDBY or ZERO CHECK operating stage.
2. To record the values for the zero signal, select SERVICE VIEW (TECHNICAL).
3. In the ONLINE VIEW, concentration after zeroing should be  $< 0.01 \text{ mg/m}^3$ . If the value exceeds  $0.05 \text{ mg/m}^3$ , massive pollution occurred during the test run and/or the device has been operated over a very long period without switching into the STANDBY operating state. In

this situation, the windows have to be cleaned (see Regular Maintenance, Section 9.2.5).

4. During each measurement, the primary signal is automatically corrected with the zero value (baseline correction).

## 9.2 Quality Assurance Procedures

To ensure that quality data are being collected the following procedures should be considered.

### 9.2.1 Resonance Test

The system automatically performs a check of the resonance frequency of the microphone in the measuring cell at the end of the operating state PAUSE. A manual execution of this function can be performed from the same operating state for a repeated check.

1. Select the menu item SERVICE/MAINTENANCE → SERVICE TESTS → RESONANCE TEST → START RESONANCE TEST.
2. At the end of the test, values should be as follows:
  - Resonance frequency: ~ 4100 Hz.
  - Max. raw meas. value: 230–30 mV.
  - Measuring cell temp. at test: ~ 52 °C.

### 9.2.2 Linearity Check of Microphone

This check can be initiated from the operating states SLEEP and PAUSE.

1. Select the menu item SERVICE/MAINTENANCE → LINEARITY CHECK → START LINEARITY CHECK.
2. When the linearity check is completed, the regression coefficient is displayed and should be higher than 0.95. Smaller regression coefficients indicate a loudspeaker or microphone fault.

### 9.2.3 Linearity Check of Laser

This check can be called from the SLEEP operating state.

1. Install the absorber window (see Section 9.1.1).

2. Select the menu item SERVICE/MAINTENANCE → LINEARITY CHECK → LINEARITY CHECK LASER → START LINEARITY CHECK LASER.
3. When the linearity check is completed, the regression coefficient is displayed and should be higher than 0.95. Smaller regression coefficients indicate a laser or laser driver fault.

#### **9.2.4 Calibration of Conditioning Unit**

Calibration is automatically carried out during every change from SLEEP to PAUSE. A manual execution of this function is used for a repeated check and can be called from operating states PAUSE and READY.

Select the menu item SERVICE/MAINTENANCE → CONDITIONING UNIT CALIBRATION → START CALIBRATION.

#### **9.2.5 Regular Maintenance**

9.2.5.1 Replace the fine filters (MM0336) in the measuring device (three filters) and the conditioning unit (one filter) when the soot layer is visible or error 28 appears (flow warning). Turn the transparent cover of the filter housing counterclockwise and remove the cover and the fine filter. Replace the fine filter and reassemble the filter housing.

9.2.5.2 Purge or replace the sampling lines when significant pollution is visible. Automatic purging is performed at each transition from the operating state SLEEP to PAUSE. If the tube (inlet on the front of the measuring device, Figure F-2 [3]) is still evidently polluted after it has been purged, it must be replaced.

9.2.5.3 Clean the measuring cell and glass tube in the measuring cell when the zero signal exceeds a value of 1.5 mV (error code 25).

1. Wear soft cotton gloves when performing the cleaning procedures.
2. Switch off the measuring device and open the lid.
3. Remove the five screws of the measuring cover and lift off the cover.
4. Remove the measuring cell windows on both sides (Figure F-5 [1] and [2]) by turning the quick lock.

5. Gently clean both measuring windows with a new cleaning cloth (HP0206).
6. Insert a cotton tip (HP0207) into the glass tube on the right-hand of the measuring cell.
7. Clean the glass tube by moving the cotton tip back and forth.
8. Remount both measuring cell windows and close the cover.
9. Retighten the five screws and close the lid.

9.2.5.4 Perform a leak check after each new installation and commissioning of the device. This operation can be performed from the SLEEP and PAUSE operating states.

1. Close the entry of the sampling line or the sampling probe.
2. In the software, select menu item SERVICE/MAINTENANCE → SERVICE TESTS → LEAK CHECK → START LEAK CHECK.
3. The green color next to the leak rate and leak rate conditioning unit values appears when the leak check is passed.

## 10.0 REFERENCES

Schindler, W., Haisch, C., Beck, H. A., Niessner, R., Jakob, E., & Rothe D. (2004). A photoacoustic sensor system for time resolved quantification of diesel soot emissions. SAE 2004-01-0968.

## 11.0 ATTACHMENTS

### 11.1 Technical Data for Equipment

#### AVL MICRO SOOT SENSOR

**Measured quantity**

Soot concentration ("elementary carbon") <50 mg/m<sup>3</sup>

**Display resolution (digital)**

0.001 mg/m<sup>3</sup>

**Data rate**

Digital: max. 5 Hz

Analog: 100 Hz

**Noise**

≤ 0.01 mg/m<sup>3</sup> (defined as 3 times the standard deviation (SD) of the measurement variation of the zero signal [clean, filtered air] with 1 s data smoothing)

**Resolution of the measurement value**

≤ 0.01 mg/m<sup>3</sup> (defined as 3 times the SD of the measurement variation of the zero signal [clean, filtered air] with 1 s data smoothing)

**Drift**

≤ 0.01 mg/m<sup>3</sup> per hour (defined as change of the average of the zero signal [clean, filtered air] over 1 h)

**Voltage supply**

230 V AC version, 50/60 Hz

Power consumption: 500 VA max.

Fuses: 2 × 5 A T (slow blow)

100/115 V AC version, 50/60 Hz

Power consumption: 500 VA max.

Fuses: 2 × 10 A T (slow blow)

**Fuses (main board)**

F1: 3.15 A T (slow blow)

F2: 6.3 A T (slow blow)

F3: 3.15 A T (slow blow)

F4: 5 A T (slow blow)

F5: 1 A T (slow blow)

F6: 3.15 A T (slow blow)

F7: 5 A T (slow blow)

**Ambient temperatures**

Operation: 5 ... 43 °C

Storage: -5 ... 70 °C (other temperature ranges on request)

**Humidity during operation**

Corresponding to a humidity of maximum 95 % at 25 °C.

If this cannot be achieved, clean and dry shop air must be supplied at the relevant connector of the device.

**Protection class**

IP34

**Tolerance of the exhaust input pressure**

-50 ... +50 mbar

**Permissible exhaust temperature at the inlet**

+20 ... +60 °C

**Humidity of the measured exhaust gas**

max. 90 % at ≤ 52 °C, non-condensing

**Dimensions**

Measuring unit: 19" × 5 HU × 530 mm (W × H × D)

Pump unit: 19" × 4 HU × 320 mm (W × H × D)

**Weight:** Measuring unit: approx. 20 kg

**AVL EXHAUST CONDITIONING UNIT**

**Output**

Dilution ratio (DR)

**Dilution ratio (DR)**

2 ... 20

**Exactness DR**

max. ±3 % in the range dilution ratio (DR) = 2 ... 10

max. ±10 % in the range dilution ratio (DR) = 10 ... 20

**Interfaces**

CAN bus

DIO

Analog Out

RS-232

**Shop air input**

1 ± 0.2 bar (rel.)

Flow: > 4 l/min

**Voltage supply**

230 V AC version, 50/60 Hz

Power consumption: 500 VA max.

Fuses: 2 × 5 A T (slow blow)

100/115 V AC version, 50/60 Hz

Power consumption: 500 VA max.

Fuses: 2 × 10 A T (slow blow)

**Fuses (main board)**

F1: 5 A T (slow blow)

F2: 3.15 A T (slow blow)

F3: 5 A T (slow blow)

F4: 5 A T (slow blow)

F5: 1 A T (slow blow)

**Ambient temperatures**

Operation: 5 ... 40 °C

Storage: -5 ... 70 °C

**Protection class**

IP34

**Dimensions**

AVL Exhaust Conditioning Unit: 19" × 4 HU × 530 mm (W × H × D)

**Weight**

Measuring unit: approx. 15 kg

**PRESSURE REDUCING UNIT**

**Maximum exhaust gas temperature**

up to 1000 °C (<1 min), 600 °C (continuous operation)

**Maximum exhaust gas backpressure**

up to 2000 mbar (rel.)

**Pressure pulsations**

±1000 mbar, but max. 50 % of exhaust gas backpressure

**Blown-off quantity**

~ 20 l/min at 1000 mbar and 600 °C

**Weight**

2 kg

## 11.2 Data Form Sample

```
#####  
### Micro Soot Sensor Log-File ###  
### Log-File-Version: 1.0 ###  
### Firmware-Version: V1.30 ###  
### DUI-Version: 2.0 ###  
### Serial number: S/N0273 ###  
### Log-File  
started:  
1/11/11          2:09:23 PM ###  
### ----- ###  
### Y_y_GasTemp [°C] ###  
### Y_y_M_NSABs [mV] ###  
### Y_y_M_Concentration [mg/m3] ###  
### Y_y_AbsPressure [mbar] ###
```

```
### Y_y_Flow [l/min] ###
### ----- ###
### State description ###
### 0...invalid ###
### 1...valid ###
### 2...valid under reservation ###
#####
```

Date [dd/mm/yy]	Time [hh:mm:ss.t]	Concentration sensor [mg/m3]	Absolute pressure [mbar]	Flow [l/min]	Zero signal [mV]	Gas temperature [°C]
1/11/2011	09:24.8	-0.007	950	1.96	0.232	45.1
1/11/2011	09:25.8	0	952	1.96		45.2
1/11/2011	09:26.8	-0.001	953	1.96	0.231	45.2
1/11/2011	09:27.8	0	953	1.96	0.231	45.2
1/11/2011	09:28.8	0	952	1.96	0.231	45.2
1/11/2011	09:29.8	0	952	1.96	0.231	45.1
1/11/2011	09:30.8	-0.001	953	1.96	0.231	45.2
1/11/2011	09:31.8	-0.001	953	1.96	0.231	45.2
1/11/2011	09:32.8	0	952	1.96	0.231	45.2
1/11/2011	09:33.8	0	953	1.96	0.231	45.1
1/11/2011	09:34.8	-0.001	953	1.96	0.231	45.2
1/11/2011	09:35.8	-0.001	952	1.96	0.231	45.2
1/11/2011	09:36.8	0	952	1.96	0.231	45.2
1/11/2011	09:37.8	0	953	1.96	0.231	45.2

### 11.3 Error and Warning Codes and Descriptions

#### 11.3.1 Errors

Error code	Description	Action
1	ADC hardware error	Device stays in "Power On" or BUSY, SLEEP is not reached. Replace the main board.
2	EEPROM hardware error	Device stays in "Power On" or BUSY, SLEEP is not reached. Replace the main board.
3	Checksum error EE-PROM	Device stays in SLEEP. No other operating states selectable. Calibration required.
4	Laser diode error	Device is switched to the operating state SLEEP.
5	Pressure(s) out of limit	Device switches solenoid valve MV_in to "zero air in" (from MEASUREMENT to ZERO CHECK).
6	Gas humidity and/or -temperature out of limit	Device switches the solenoid valve MV_in to "zero air in". Check the condition of the sample gas (too cold / too wet?).
7	Error thermoelectric cooler	Device is switched to the operating state SLEEP.
8	Monitoring photodiode intensity too low	Device is switched to the operating state SLEEP. Problems with the fiber-optic cable or the collimator suspected, bad window pollution.
9	Measuring chamber cover open	Laser cannot be switched on. User action: Switch off the voltage supply and/or close the measuring chamber cover.
10	Humidity at the thermoelectric cooler too high	Laser is switched off, device switches to the operating state PAUSE. User action: Supply dry, clean air to the purge air inlet.
11	Measurement value too high	Device switches solenoid valve MV_in to "zero air in" (from MEASUREMENT to ZERO CHECK).
12	Time-out measuring cell heating	Device cannot switch to the operating state STAND-BY or PAUSE and therefore switches to SLEEP.
13	Driver error thermoelectric cooler	Laser cannot be switched on.
101	ADC hardware error	Device stays in "Power On" or BUSY, SLEEP is not reached. Replace the main board.
102	EEPROM hardware error	Device stays in "Power On" or BUSY, SLEEP is not reached. Replace the main board.
103	Checksum error EE-PROM	Device stays in SLEEP. No other operating states selectable. Calibration required.
104	MFD communication error	Device stays in the relevant operating state. Firmware independently tries to reestablish communication. In connection with this error, error codes 107 and 125 may be displayed as well.

105	Up to firmware version 1.10: MFM and/or MFC time-out	Device stays in the relevant operating state. Firmware independently tries to reestablish communication. In connection with this error, error codes 107, 121 and 125 may be displayed as well.
	As of firmware version 1.11: MFC time-out	Device stays in the relevant operating state. Firmware independently tries to reestablish communication. In connection with this error, error codes 107 and 125 may be displayed as well.
106	MFD conditioning time-out	Device cannot switch to the operating state STAND-BY or PAUSE and therefore switches to SLEEP.
107	No dilution air available	This error is reported when switching either from PAUSE to STAND-BY or from STAND-BY to MEASUREMENT. Device stays in the relevant operating state.
108	CO <sub>2</sub> sensor time-out	Device stays in the relevant operating state. Firmware independently tries to reestablish communication.
109	MFM time-out (as of firmware version 1.11)	Device stays in the relevant operating state. Firmware independently tries to reestablish communication. In connection with this error, error code 121 may be displayed as well.

### 11.3.2 Warnings

Error code	Description
21	Device parameter warning Permanently stored calibration parameters might be invalid (see also APAR on page 160).
22	Service warning (after 1000 operating hours)
23	Zeroing warning
24	Low voltage of the buffer battery on the main board
25	Window pollution too large
26	Leak check failed
27	Resonance test error
28	Flow warning (flow through measuring cell too low or too high)
29	Electronic equipment temperature too high
30	Sampling line temperature out of limit
31	Measuring cell temperature out of limit
32	Voltage supply error The internal voltages can be checked with AADC.
119	Relative calibration too high
120	MFC flow out of limit (0 ... 5458 ml/min)
121	MFM flow out of limit (0 ... 5458 ml/min) or $\pm 10$ % of current mean value averaged over 10 s in operating state MEASUREMENT
122	Service warning (after 1000 operating hours)
123	Error during relative calibration
124	Low voltage of the buffer battery on the main board
125	No dilution air available (warning in operating state PAUSE)
126	Dilution cell temperature out of limit
127	Dilution ratio too high
128	Target flow for dilution air not reached
129	Electronic equipment temperature too high
130	Sampling line temperature out of limit
131	MFD temperature out of limit
132	Voltage supply error The internal voltages can be checked with AADC (directly on the COM1 serial port of the AVL Exhaust Conditioning Unit).

# Appendix G: Sampling and Measurement of Nonvolatile Particulate Matter Mass Using the Filter-Based Gravimetric Method

STANDARD OPERATING PROCEDURE 2103

NRMRL/APPCD

APPROVED: August 18, 2011



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## 1.0 SCOPE AND APPLICATION

This standard operation procedure (SOP) provides instructions on collecting and measurement of nonvolatile particulate matter (nvPM) mass using the standard filter-based gravimetric method. The existing procedures described in Title 40 Parts 1065 and 86 of the Code of Federal Regulations (CFR) are used as guidance for the PM sampling and filter weighing procedures of the SOP.

This SOP is a step-by-step procedure that describes how to perform the sampling and weighing of the filters (loaded with PM and unloaded) as well as to analyze the data and perform all necessary calibrations and calculations.

## 2.0 METHOD SUMMARY

Preconditioned and preweighed polytetrafluoroethylene (PTFE) filters (Whatman catalog no. 7592-104 or equivalent) are used to collect the nvPM mass from the main sample stream at a flow rate of approximately 50 L/min. The filters are post-conditioned and weighed, and the PM mass collected on them is used as a reference mass to evaluate other PM mass collection methods (e.g., multi-angle absorption photometry; laser-induced incandescence, photoacoustic analysis, and filter sampling with carbon burn-off) employed during the same experiments.

A prebaked quartz-fiber filter (QFF) is used as a backup filter placed in line after the PTFE filter. After sampling, the QFFs are analyzed using the procedure described in SOP 2104 and therefore that procedure is not repeated here. Studies have found that QFFs can adsorb the semivolatile organic carbon (OC) (Turpin et al., 1994) in addition to the PM OC (positive sampling artifacts). Therefore, the semivolatile OC mass measured on the backup filter is used to correct for the total OC measured, as described in SOP 2104.

## 3.0 DEFINITIONS

**Organic carbon (OC):** Optically transparent carbon at approximately 670 nm removed (through thermal desorption or pyrolysis) and char deposited when heating a filter sample to a preset maximum (850 °C) in a non-oxidizing (helium) carrier gas.

**Nonvolatile PM (nvPM):** Particle emissions that exist at gas turbine engine exit plane temperature and pressure conditions and that do not contain volatile particle contributions that condense at lower temperatures.

#### 4.0 INTERFERENCES

Personnel should avoid activities that could contribute to free airborne particles or static electricity. Particular attention should be given to clothing worn when preparing or weighing filters. Many cloth materials and clothing items have been shown to contribute significantly to static effects. These include lab coats and wool sweaters, pants, and shirts and clothes made of polyester, acrylic, or nylon. In addition, avoid dirty or dusty clothing, cut-off blue jeans, soft Vibram-soled shoes, and rubber-soled sneakers. Recommended clothing includes non-aged or non-brushed denim, cotton twill weave pants and shirts, 100% cotton shirts or sweat shirts, and hard-soled leather shoes.

#### 5.0 EQUIPMENT AND SUPPLIES

- Vacuum pump suitable of providing approximately 45 L/min.
- Two 47-mm stainless steel filter holders meeting Title 40 CFR Part 1065, Subpart B, requirements.
- 47-mm PTFE filters (Whatman catalog no. 7592-104 or equivalent) with associated cassettes meeting Title 40 CFR Part 1065, Subpart B, requirements.
- 47-mm prebaked quartz-fiber filters (Tissuequartz™ 2500 QAT-UP, 47 mm from Pall Corporation catalog no. 7202 or equivalent) with associated cassettes.
- Orifice flow meter incorporating 9.53-mm (3/8-in.) outside diameter (OD) inlet/outlet fittings and differential pressure (dP) cell (Omega Model PX658-10D5V or equivalent), including plastic isolation valves and tubing for interconnection, calibrated by the APPCD Metrology Laboratory according to MOP FV-0201.1 within 1 year of use. Orifice meter readings are recorded by a computerized data acquisition system (DAS) running the DasyLab® software package.
- Absolute pressure transducer (Omega Model PX309-015A5V or equivalent) calibrated by the APPCD Metrology Laboratory according to MOP PR-0400.0 within 1 year of use. Absolute pressure readings are also recorded by the DAS.
- Brass or stainless steel three-way switching valve with 9.53-mm (3/8-in.) OD fittings.
- Two-way brass or stainless steel needle valve with 9.53-mm (3/8-in.) OD inlet/outlet fittings.
- Approximately 1 meter of 9.53-mm (3/8-in.) OD stainless steel or Teflon sampling line to interconnect the above components downstream of the filter holder.
- Tweezers (for manipulation of PTFE [with grounding strap] and quartz filters).
- Analytical microbalance with 1- $\mu$ g readability and 5-g capacity (Sartorius ME5 or equivalent) installed in a temperature- and humidity-controlled weigh room (see

specifications below). The microbalance shall be recertified by the APPCD Metrology Laboratory within 1 year of use.

- Class 1 calibration weights.
- Aluminum foil.
- Sterile Petri dishes (Pall Corporation catalog no. 7242 or equivalent).
- Static eliminator consisting of two polonium-210 units (Nuclespot P-2042 from NRD, USA or equivalent) positioned upside down on stainless steel holders and separated by approximately 1 inch.
- Cassette separator – anodized aluminum (Airmetrics, USA catalog no. 600-007 or equivalent).
- Cassette mailers – antistatic (Airmetrics, USA catalog no. 600-008 or equivalent).
- Powder-free nitrile gloves.
- Laboratory timer with 1-s resolution.
- NIST-traceable barometer certified by the APPCD Metrology Laboratory within 1 year of use.
- Environmental weighing chamber meeting the specifications outlined in Section 6.1.

## 6.0 PROCEDURES

### 6.1 Weighing Room Specifications

Design and specifications of the weighing room should meet those listed in Title 40 CFR Part 50, Appendix L, Section 8.0. The ambient conditions within the room should be maintained at an average temperature of 20–23 °C and a mean relative humidity (RH) of 30–40%. Control of the internal environment should be maintained within  $\pm 2$  °C and  $\pm 5\%$  RH as measured over a 24-h period.

Verification of the temperature and RH specifications must be certified at least annually using NIST-traceable standards per the EPA document *Quality Assurance Guidance Document 2.12: Monitoring PM<sub>2.5</sub> in Ambient Air Using Designated Reference or Class I Equivalent Methods*.

To isolate the balance from external noise and vibration, it should be mounted on a vibration-isolation platform. Static electric charge in the balance environment should be minimized with use of an electrically grounded balance, 300 series stainless steel grounded tweezers for handling filter media, and electrically grounded, static-electricity neutralizers for the sampling media.

## 6.2 Preconditioning and Tare Weighing of PTFE Filters

### 6.2.1 *Preconditioning*

Before weighing filters, take the following steps to prepare the PTFE filters, weighing environment, and equipment:

1. Write down the date/time, temperature, pressure and RH in the weighing room before measurement.
2. The ambient temperature of the room should be maintained at  $20\text{w}-23 \pm 2$  °C over 24 h. The RH should be maintained at  $30-40\% \pm 5\%$  over 24 h.
3. To avoid contamination, remove any unnecessary items and clean any dirty areas.
4. Put on powder/static-free latex gloves and any necessary garments needed to minimize human-produced contamination while handling filters.
5. Use a Kimwipe (or equivalent low-particulate wipe) to wipe the areas where forceps, filters, and Petri dishes will be placed and around the balance. Wipe the forceps that will be used for filter handling.
6. All new filters should be equilibrated prior to weighing. They should also be inspected for holes or other defects prior to use. This can be done by holding the filter up to the light with forceps and looking for holes. If the new filter passes inspection, place it in a numbered (labeled) Petri slide. Arrange new filters in sets (e.g., sets of 10) and place them in a clean area for equilibration for a minimum of 48 h prior to obtaining tare weights. The Petri slide tops should remain partially open during the equilibration.
7. Place any filter trays, standard weights, laboratory notebooks, or any other items needed for weighing on the weighing table or within reach of the table.
8. It is required that at least two unused reference filters remain in the weighing room at all times in covered, but unsealed petri slides to verify the cleanliness of the PM-stabilization environment. These reference filters shall be placed in the same area as the sample filters. The Petri slide tops should be partially open at the same time as the sample filters for preconditioning and weighed at the same time as the sample filters. If the average weight of the reference filter pairs

changes between the clean and used sample filter weighings by more than 40  $\mu\text{g}$ , then all sample filters and background filters in the process of stabilization shall be discarded and tests repeated. The reference filter pairs should be changed at least once a month, but never between the clean and used sample filter weighings. The reference filters should be the same size and made from the same material as the sample filters.

### **6.2.2 Balance Setup**

1. Put on a pair of powder-free nitrile gloves and leave them on for the remainder of the weighing session.
2. Unload the pan, close the draft shield, and zero the microbalance. When the balance shows zero readout, press the FKey. A “C” will now be displayed. The built-in calibration weights are internally applied by servomotor and removed at the end of calibration. If external interference affects the calibration procedure, you might obtain a brief display of the error message “Err 02.” In this case, re-zero and then press the FKey again when zero readout appears. An acoustic signal indicates the end of calibration.
3. With the balance reading zero, weight the working standard weights (such as the 100 mg and 200 mg weights) and record the data, making note of the measurement units.
4. When satisfactory results are obtained from the standard weights, place the standards in their designated container, cover, and move them out of the way until the end of the weighing session when they will be used again.

### **6.2.3 Tare Weighing**

1. Arrange filters in sets (e.g., sets of 10) within easy reach of the balance to minimize unnecessary movements during the weighing.
2. Equilibrate the microbalance by opening the door for 5 s and then closing the door. Repeat this step at least three times.
3. Set up two polonium strips using the special gooseneck holder with one source positioned upside down above and aimed directly at the other. They should be approximately 1 in. apart to maximize the static-reducing effect of the polonium. Hold a filter with grounded tweezers between the sources to expose both sides of the filter at least 20 s

before moving the filter to the balance pan. It is preferable to expose all filters identically to the polonium strips and to not flip the filters for polonium exposure.

4. First weigh the reference filters to gauge the long-term stability of the weighing room. The standard for repeatability between one weighing session and the next is  $\pm 0.011$  mg for the filters/room to be “in control”.
5. Develop an organized sequence to follow for every session so that each filter gets weighed in the same fashion as the others and so that there are no mix-ups on filter ID (whether it has been weighed or not), placement on storage tray, or entries in the data log.
6. When weighing a filter, note that the balance adjusts when the filter is placed on the balance pan. Watch the display after the initial increase in numbers and watch for the unit symbol (such as g for gram, mg for milligram, or  $\mu\text{g}$  for microgram) to appear at the end of the number sequence. Once the stability symbol appears, wait 10 s. If the number has not changed within 10 s, then record the weight. If the number does change, wait another 10 s. Repeat this step until the number does not change within the 10-s interval.
7. After weighing a filter, place it in the same Petri slide and tightly close the top on the slide.
8. Close the door on the balance and allow the display to settle back to zero to check the stability of the balance. If at any time the balance fails to resettle, it must undergo the calibration process and the filters of that group must be weighed again.
9. After weighing an entire set of filters, it is necessary to reweigh a few random filters from that lot. Be sure to record this QA reweigh data, too. A minimum of two filters per 10 should be chosen by an independent operator and reweighed. If either of the two is unable to meet the previous measurement within  $\pm 0.004$  mg, the entire lot of 10 filters must be reweighed and the reweigh performed again.
10. After filter weighing is completed, reweigh the working standard weights and reference filters, record the results, and compare these measurements with the ones taken at the beginning of the weigh session. The second measurements should be within  $\pm 0.003$  mg of the first ones.

11. After weighing is completed, place the reference filters in their Petri slides, close the tops and keep them closed until new filter sets are ready for conditioning.
12. Make sure all laboratory equipment is put away, and gather all items that need to be taken out of the laboratory.
13. Write down the date/time, temperature, and RH before leaving the weighing room.

### **6.3 Preparation of Quartz-Fiber Filters**

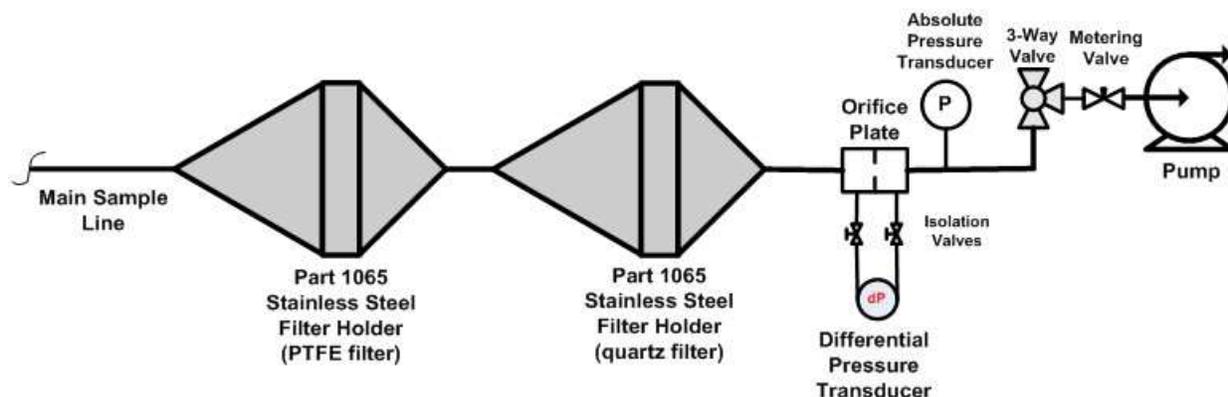
New QFFs usually have an OC background of 2 to 5  $\mu\text{g}/\text{cm}^2$ , which must be removed prior to analysis. Use the following procedure to eliminate this background for newly purchased QFFs:

1. Prebake in a muffle furnace at 550 °C for 12 h before sampling.
2. Store in Petri dishes lined with cleaned aluminum foil (also baked at 550 °C for 12 h). After baking, rinse aluminum foil in n-hexane and dry in the oven at 100 °C for 10 min. Aluminum foil liners must be cut to cover the inside surfaces of the Petri dishes so that the filters do not directly touch the dish when placed inside the lined dishes.

Filters and liners must be handled with Teflon forceps to avoid contamination.

### **6.4 Sampling Procedure**

1. Install one or more preweighed PTFE filters and prebaked quartz filters into separate filter cassettes in the laboratory while wearing nitrile gloves; transport the filter cassettes to the test location, as appropriate.
2. Assemble the sampling train as illustrated in Figure G-1 and connect this equipment to the main stainless steel sampling line provided by others.



**Figure G-1. Sampling train.**

3. Install a 47-mm filter cassette containing a preweighed PTFE filter into the front filter holder per the manufacturer’s recommendations.
4. Install a 47-mm filter cassette containing a prebaked QFF (backup filter) into the back filter holder per the manufacturer’s recommendations.
5. Conduct a leak check of the system by removing the sampling line and installing a vacuum gauge on the inlet of the PTFE filter holder. Start the pump with the three-way valve in the “bypass” (open to atmosphere) position. Before proceeding, close the metering valve and then just crack the valve to restrict the rate at which the vacuum is placed on the system to avoid tearing the filters. Close the isolation valves to the differential pressure transducer (if this is not done, the transducer can be damaged), and switch the three-way valve to the “sample” (straight through) position. Observe the vacuum gauge until the maximum vacuum is reached and then switch the three-way valve back to the “bypass” position. Observe the vacuum gauge for a period of 2 min. If the vacuum drops more than 127 mm Hg (5 in. Hg), the system has a leak. Turn off the pump and slowly release the vacuum by switching the three-way valve to the “sample” position. Once the vacuum has been released, open the isolation valves to the differential pressure transducer and remove the vacuum gauge from the sampling train inlet. If a leak is indicated, find and repair the leak and repeat the above procedure.
6. To prepare for sample collection, move the three-way valve to the “bypass” (open to atmosphere) position and start the pump. When sampling conditions become stable, switch the three-way valve to the “sample” (straight through) position and record the start time to the nearest second.
7. Sampling time is limited by requirements in SOP 2104 and the minimum detection limit of the Sunset OC/EC analyzer. Because of these limitations,

sample mass on the PTFE filter must be from 900 to 1000  $\mu\text{g}$ . At the end of a sampling period, move the three-way valve back to “bypass” and record the end time to the nearest second.

8. Stop the pump and remove the filter cassettes from the filter holders. Place them in clean, labeled cassette mailers. If another run is to be made, install fresh filter cassettes in the filter holders and repeat Steps 5 through 8.
9. Remove the PTFE filters from the cassette mailers. Place them in the originally used and labeled Petri slides, and place the QFFs in the aluminum foil-lined Petri dishes. Use the cassette separator for easy opening of the filter cassettes. QFFs should be stored in a freezer until ready for analysis.
10. Collect at least one field blank of each filter type for every 10 samples collected. A field blank consists of installing a filter into the sampling train in the normal fashion and immediately recovering it without any air passing through the filter. The field blanks should be handled and analyzed in the same manner as the samples collected (see below).

## **6.5 Post-Conditioning and Total Weighing of PTFE Filters**

- 6.5.1** Sampled PTFE filters should be brought to the balance room at least 24 h before weighing for equilibration with Petri slide tops left partially open.
- 6.5.2** The same protocol for entering and leaving should be followed including recording the pressure, temperature, and RH before entering and after exiting. At this time, also make sure the lid of the reference filter is left open for equilibration.
- 6.5.3** To weigh the total mass on the filters, repeat steps 1 through 13 in Section 6.2.3.

## **7.0 DATA ACQUISITION, CALCULATIONS, AND DATA REDUCTION**

### **7.1 Buoyancy Correction of PM Sample Media**

Given that the net PM mass is calculated by subtracting the unloaded filter mass from the sample-loaded filter mass, the two buoyancy corrections will cancel each other under normal ambient conditions (i.e., ambient pressure changes of  $\pm 10\text{--}20$  mm Hg). Thus, a buoyancy correction should be calculated only in the cases when absolute filter mass is important and of interest for the analyst. In that situation, the buoyancy correction should be calculated according to the formulas listed in Title 40 CFR Part 1065, Subpart G (1065.690).

## 7.2 Blank Correction

Final sample results should always be blank-corrected. For that purpose, two types of blanks are used: laboratory and field blanks. Laboratory blanks are preconditioned and preweighed filters stored in labeled Petri slides in the laboratory. Field blanks are preconditioned and preweighed filter subjected to all aspects of the sample collection, transportation, field handling, and preservation as a real sample. Any measured PM mass in the blank samples represents contamination and should be deducted from the real samples.

## 7.3 Net Particulate Matter Weight

The net PM weight of each filter should be equal to the corrected gross filter weight minus the corrected tare filter weight and minus any PM mass that comes from contamination and is measured on the field blank filters.

## 7.4 Average Air Flow Rate

The average flow rate of the air passing through the filter is corrected to EPA standard temperature and pressure (STP) conditions of 25 °C and 760 mm Hg. It is calculated from the orifice meter and absolute pressure and tunnel temperature readings by:

$$Q_{\text{stp}} = Q_{\text{avg}} \frac{P_a}{P_{\text{stp}}} \frac{T_{\text{stp}}}{T_a}$$

where:

$Q_{\text{avg}}$  = average flow rate calculated from the orifice meter ( $\text{m}^3/\text{min}$ )

$P_a$  = absolute pressure (mm Hg)

$T_a$  = temperature (K)

$P_{\text{stp}}$  = standard pressure = 760 mm Hg

$T_{\text{stp}}$  = standard temperature = 298.15 K

## 7.5 Concentrations of Particulate Matter in Air

The concentration of PM can be calculated from the net PM weight and the total volume of air sampled as:

$$C_{PM} = \frac{(m_f - m_t)}{Q_{stp} t}$$

where:

$C_{PM}$  = PM concentration ( $\mu\text{g}/\text{m}^3$ )

$m_f$  = corrected filter final weight ( $\mu\text{g}$ )

$m_t$  = corrected filter tare weight ( $\mu\text{g}$ )

$Q_{stp}$  = standard air flow rate through the filter as measured by the orifice meter during the sampling period ( $\text{m}^3/\text{min}$ )

$t$  = total sampling time (min)

## **8.0 QUALITY CONTROL AND QUALITY ASSURANCE PROCEDURES**

### **8.1 Laboratory and Field Blanks**

Laboratory and field blanks are run in parallel with each sample to eliminate contamination that comes from the same environments where the sample filter is exposed.

### **8.2 Reference Filters**

Reference filters are filters that remain in the weighing room on the same place and over the same preconditioning time as the sample filters. The purpose of these filters is to verify the cleanliness of the PM stabilization environment and to detect any unusual events that might have effects on PM mass on sample filters.

### **8.3 Balance Performance Verification**

Balance performance must be verified:

- At least once a year by the APPCD Metrology Laboratory.
- Before weighing any filter by zeroing and spanning the balance with at least one calibration weight.
- Before and after filter weighing session by weighing reference PM sample filters.

### **8.4 Reweighing of Filters**

After weighing the entire set of filters, 20 % of them are subjected to reweighing. If any reweighs do not meet the previous measurement within  $\pm 0.004$  mg, the entire set of filters must be reweighed. Following the same procedure, an independent person should reweigh 10 % of all filters and record the weights. Any reweighs that do not meet the repeatability criteria of  $\pm 0.004$  mg require that all filters in that respective set should be reweighed.

## 9.0 REFERENCES AND SUPPORTING DOCUMENTATION

Code of Federal Regulations (CFR), Title 40: Protection of Environment; Part 1065 – Engine testing procedures.

Code of Federal Regulations (CFR), Title 40: Protection of Environment; Part 86 – Control of emissions from new and in-use highway vehicles and engines (continued).

Sampling and measurement of non-volatile particulate matter mass using the thermal/optical – transmittance carbon analyzer. SOP No. 2104, U. S. Environmental Protection Agency, National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, Research Triangle Park, NC, 2011.

Turpin, B. J.; Huntzicker, J. J.; Hering, S. V. (1994). Investigation of organic aerosol sampling artifacts in the Los Angeles Basin. *Atmos. Environ.*, 28, 3061-3071.

Calibration of Gas Flow Rate Measurement Devices Using the DHI Molbox/Molbloc™ System. MOP No. FV-0201.1, U. S. Environmental Protection Agency, National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, Research Triangle Park, NC, 2008.

General Procedure for Calibrating/Evaluating Pressure Measurement Devices Using the Mensor APC600 Automated Pressure Calibrator. MOP No. PR-0400.0, U. S. Environmental Protection Agency, National Risk Management Research Laboratory, Air Pollution Prevention and Control Division, Research Triangle Park, NC, 2009.

Quality Assurance Guidance Document 2.12: Monitoring PM<sub>2.5</sub> in Ambient Air Using Designated Reference or Class I Equivalent Methods. U. S. Environmental Protection Agency, National Exposure Research Laboratory, Human Exposure and Atmospheric Sciences Division, Research Triangle Park, NC, November 1998.

# Appendix H: Operation of the TSI Scanning Mobility Particle Sizer (SMPS) Model 3936

MISCELLANEOUS OPERATING PROCEDURE 1412

NRMRL/APPCD



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## **1.0 SCOPE AND APPLICATION**

This procedure is for experiments conducted using the TSI (Shoreview, MN, USA) Model 3936 Scanning Mobility Particle Sizer (SMPS) and Aerosol Instrument Manager (AIM) Version 5.2 software. The purpose of this document is to provide a written and repeatable procedure for the operation of the SMPS using the AIM software.

## **2.0 METHOD SUMMARY**

The Model 3936 SMPS consists of the Model 3080 electrostatic classifier (EC), the Model 3025A condensation particle counter (CPC), and associated plumbing. This facility currently uses two 3936 SMPS systems, one with a long differential mobility analyzer (DMA) Model 3081 and another with the nano-DMA Model 3085. Both systems are covered in this document.

For more specific and detailed information relating to the setup, operation, and maintenance of this instrument, refer to the Model 3936 SMPS Instruction Manual. This manual is stored with the instrument.

## **3.0 INSTRUMENT AND SOFTWARE SETUP**

### **3.1 Instrument Setup**

1. Turn on the CPC and EC.
2. Set analog output to HOST on the CPC.
3. Set the voltage control to “Analog Ctrl” on the EC.
4. Turn the TSI SMPS 3936 on and allow at least 30 min. for warm-up.
5. Set aerosol and sheath flow rates as appropriate by referring to the Recommended Operating Parameters table located on page 4-4 of the Model 3936 SMPS Instruction Manual.
6. Perform a SMPS system check, which can be found on pages 4-6 and 4-7 of the Model 3936 SMPS Instruction Manual.

The instrument is ready for sampling after the TSI SMPS software is set up.

### **3.2 Software Setup**

1. Open the AIM Version 5.2 software.
2. Select File/New and enter the file name.
3. Select Open or press Enter.

4. Select File/Properties OR Run/Properties and verify or enter the following SMPS Properties:

Hardware Settings

Classifier Model	3080
Impactor Type	Enter cut point for serial no. of impactor
CPC Model and Flow Rate	3025A
DMA Flow Rate (L/min):	
Sheath	6 L/min (default)
Aerosol	0.6 L/min (default)
Scan Time (s):	
Up	150 (adjust based on size range)
Retrace	30
Size Range Bounds (Diameter)	Select “Set to Max Range” button

Scheduling

Scans per Sample	1
Number of Samples	120

Physical Properties

Gas Properties	Select “Set to Defaults for Air” button
Particle Density (g/cc)	As appropriate for the aerosol (nominally=1)
Multiple Charge Correction	“On”
Title	As appropriate for the experiment
Instrument ID	As appropriate
Comments	As needed

5. Select OK or press Enter.
6. Select View / Size Data / Graph.
7. Select View / Units / Concentration (dW).
8. Select View / Weight / Number.
9. Select Format / Channel Resolution / (32 or 16) channels/decade.

10. Select Run / Auto Export to File and enter the following Dialog properties:

Data Types            Number / Concentration (dW)

Delimiter            Comma

11. Select OK or press Enter.

12. Enter the Export As properties:

Save in:              Create directory if necessary

Save as type:        Delimited text file (.txt)

File name:            Create Filename

13. Select Save or press Enter.

## **4.0 DATA COLLECTION**

### **4.1 Start Data Collection**

After choosing the Run / Start data collection command, there is an approximate delay of 4 s before data collection begins. (As an example, to start data collection at 11:10:00, select the Start data collection command at 11:09:56).

### **4.2 Stop Data Collection**

1. Select Run / Finish current sample.
2. Select File / Save.
3. Select File / Close.

### **4.3 Instrument Software Shutdown**

Select File / Exit.

### **4.4 Instrument Hardware Shutdown**

Standard practice is to keep the SMPS operating unless an extended period of inactivity is expected.

1. Turn OFF the system vacuum pump.
2. Turn Off the classifier (switch is located on the back).
3. Unplug the CPC.

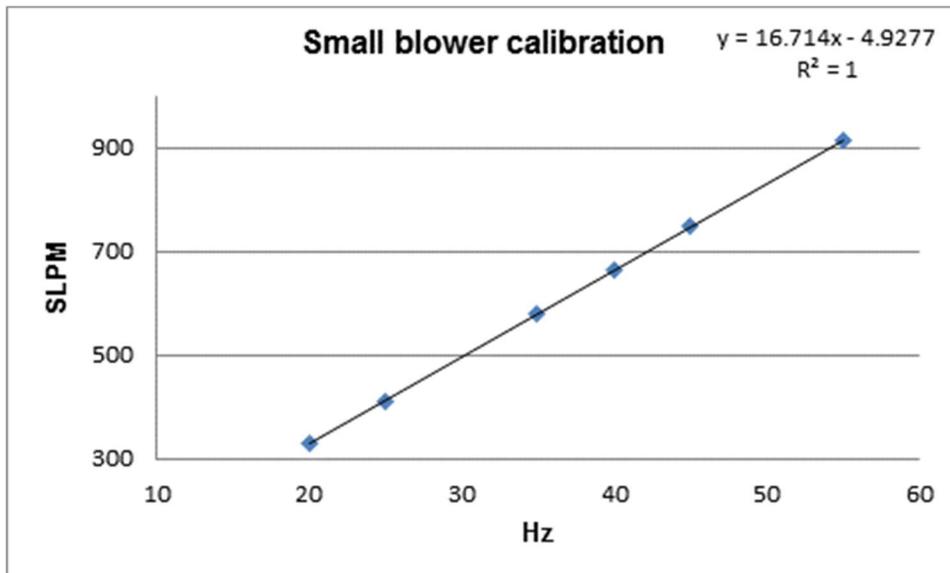
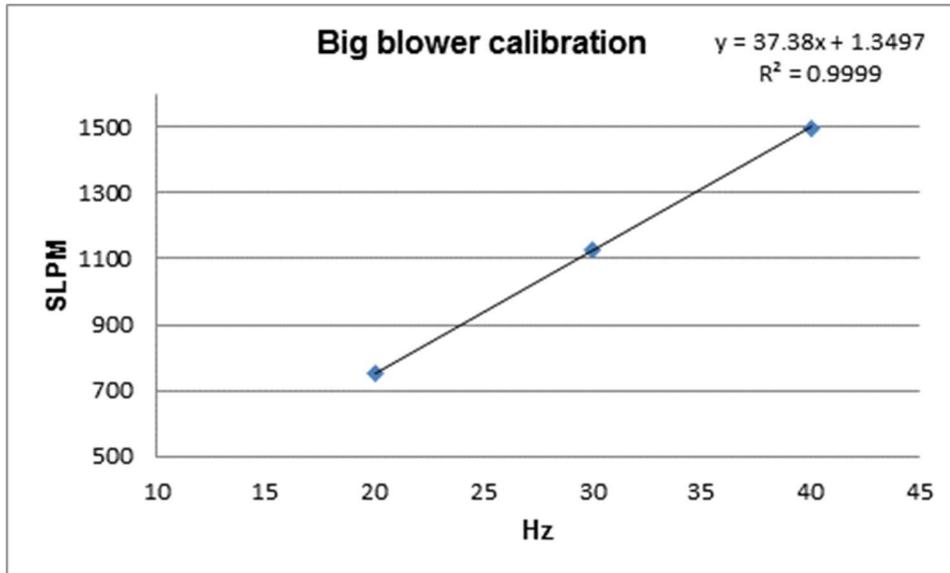
## **5.0 DATA PROCESSING**

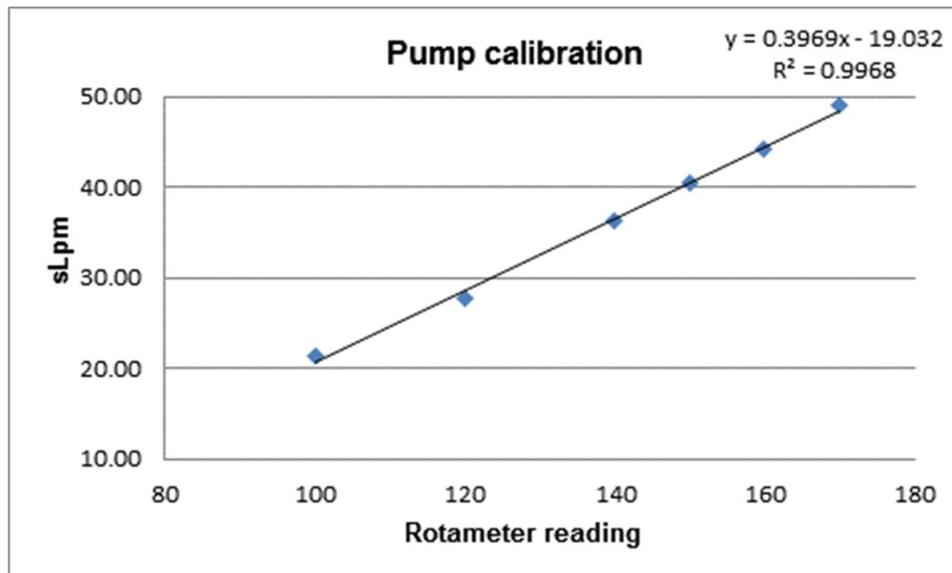
The AIM software writes data into two files: raw data (with extension \*.S80) and display format (with extension \*.P80). Raw data is exported as it is collected into a comma-delimited text file format. Raw data files and processed (exported) data files are managed per instructions contained in the appropriate QAPP/test plan. In general, raw data and exported text files are transferred from the instrument computer to a central computer. Data transfer is a simple drag and drop procedure. Processed data is generated from the exported text file using Microsoft Excel.

# Appendix I: Blowers/Pump Calibration Curves



The x-axis represents blower reading (Hz) or pump adjustment (rotameter reading) and the y-axis the calibrated standard volume of air passing through the tunnel at that condition.





# Appendix J: Experimental Verification of LII Recalibration and SuperMAAP Flow Adjustment and Software Changes



After completing the baseline study, several issues were discovered with the LII and SuperMAAP that required further investigation and corrective action. This investigation revealed that the following were needed: corrections to the data to reflect new calibration constants for the LII, a slight flow adjustment and software change for the SuperMAAP, and minor temperature corrections to the Micro Soot Sensor (MSS) data. After these corrections were made to the entire data set, a limited evaluation was conducted in the laboratory to compare the post-processed data to new experimental data obtained after implementation of the necessary changes to the LII and SuperMAAP. For the LII, this evaluation involved three repeat tests at 50 and 500  $\mu\text{g}/\text{m}^3$ , both with and without use of the catalytic stripper (CS), the results of which were compared to the corrected data for the same experimental conditions in the baseline study. The results of the experimental verification are provided below. Note that these data have not been corrected for the SuperMAAP filter change problem discussed in Appendix C.

## 1.0 VERIFICATION OF LII RESULTS

To validate the LII post-processing method, the post-processed results provided by Artium Technologies were compared to new experimental data collected at target concentrations of 50 and 500  $\mu\text{g}/\text{m}^3$  as shown in Figures J-1 and J-2. The LII data were plotted against the organic carbon (OC)-corrected Teflon filter results in Figure J-1 and the NIOSH Method 5040 results in Figure J-2 for experiments conducted with and without use of the CS. As can be seen from Figure J-1 for Teflon filter data, a difference of 6 to 19 % in slope was observed between the post-processed results and the new experimental data, depending on CS use. For the comparison against NIOSH in Figure J-2, the difference ranged from 6 to 12 %, again depending on CS operation. It should also be noted that the MiniCAST was repaired shortly before performing experiments with the CS, which probably had at least some influence on the LII measurement results. The average OC/total carbon (TC) ratio was approximately 69 % before MiniCAST servicing and approximately 81 % after (during repeated CS experiments) using the same operating parameters. The other instruments (MSS and NIOSH 5040) did not register any significant changes in the slope before and after MiniCAST repair, however.

Although the comparison of experimental to post-processed data was not as good as expected for the stripped MiniCAST aerosol, the unstripped aerosol produced slopes within 6 % regardless of whether the comparison was against the OC-corrected Teflon filter results or the NIOSH 5040 results, indicating good agreement. These results would suggest that there should be little problem using post-processed data. For the data with use of the CS, the deviation in slope was 12 to 19 % and thus not as good as for the unstripped aerosol. In this case, a change in the MiniCAST exhaust particles after servicing might have caused changes in the operation of the stripper, thus negatively

impacting the data obtained. As discussed in the main text, the stripper did not provide anywhere near the expected OC reduction and its operation was found to be highly idiosyncratic. For this reason, we considered the post-processed LII stripper data to be adequate for use without repeating the entire experimental matrix.

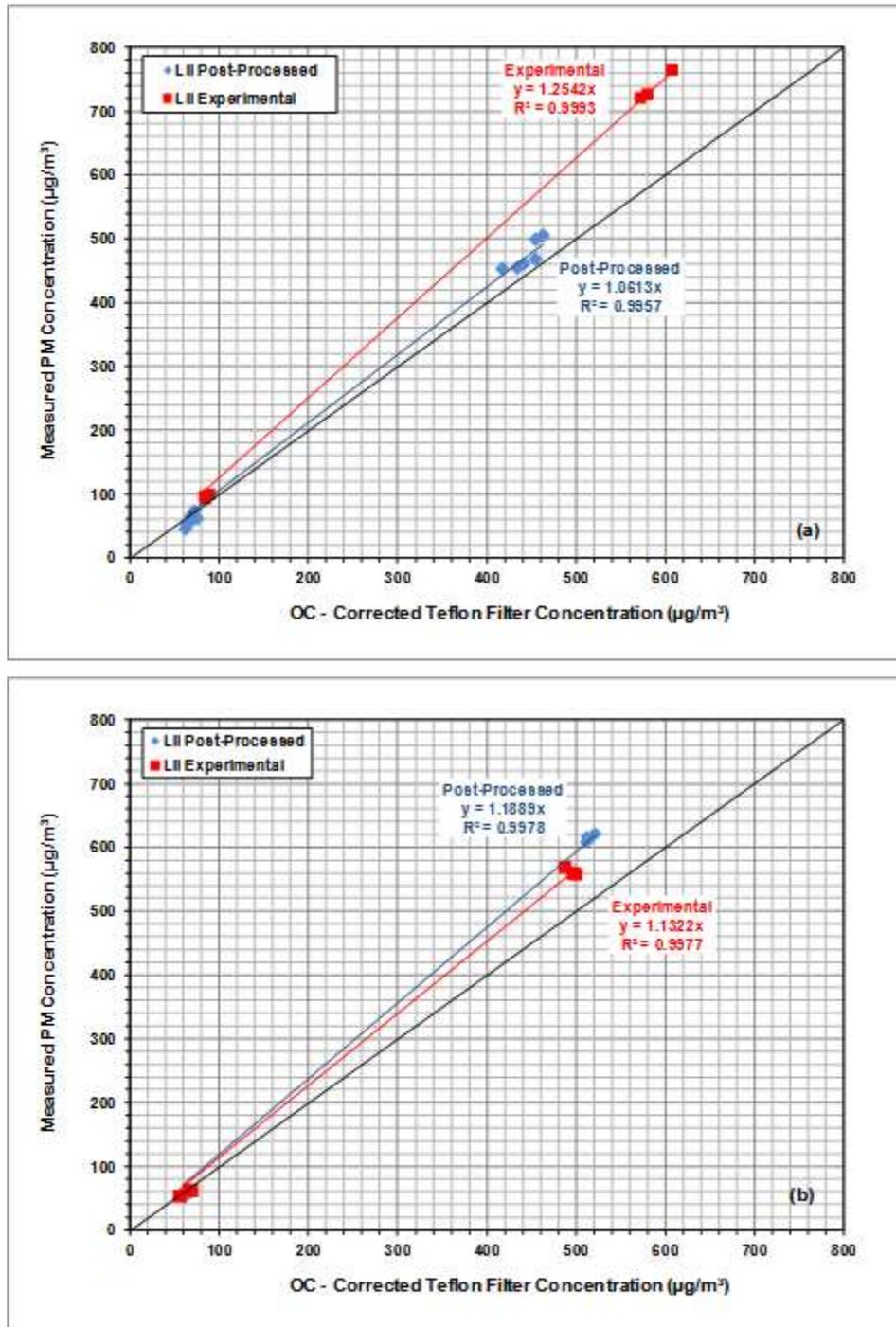


Figure J-1. Comparison of LII post-processed data to new experimental results based on Teflon filter measurements for tests (a) with stripper and (b) without stripper.

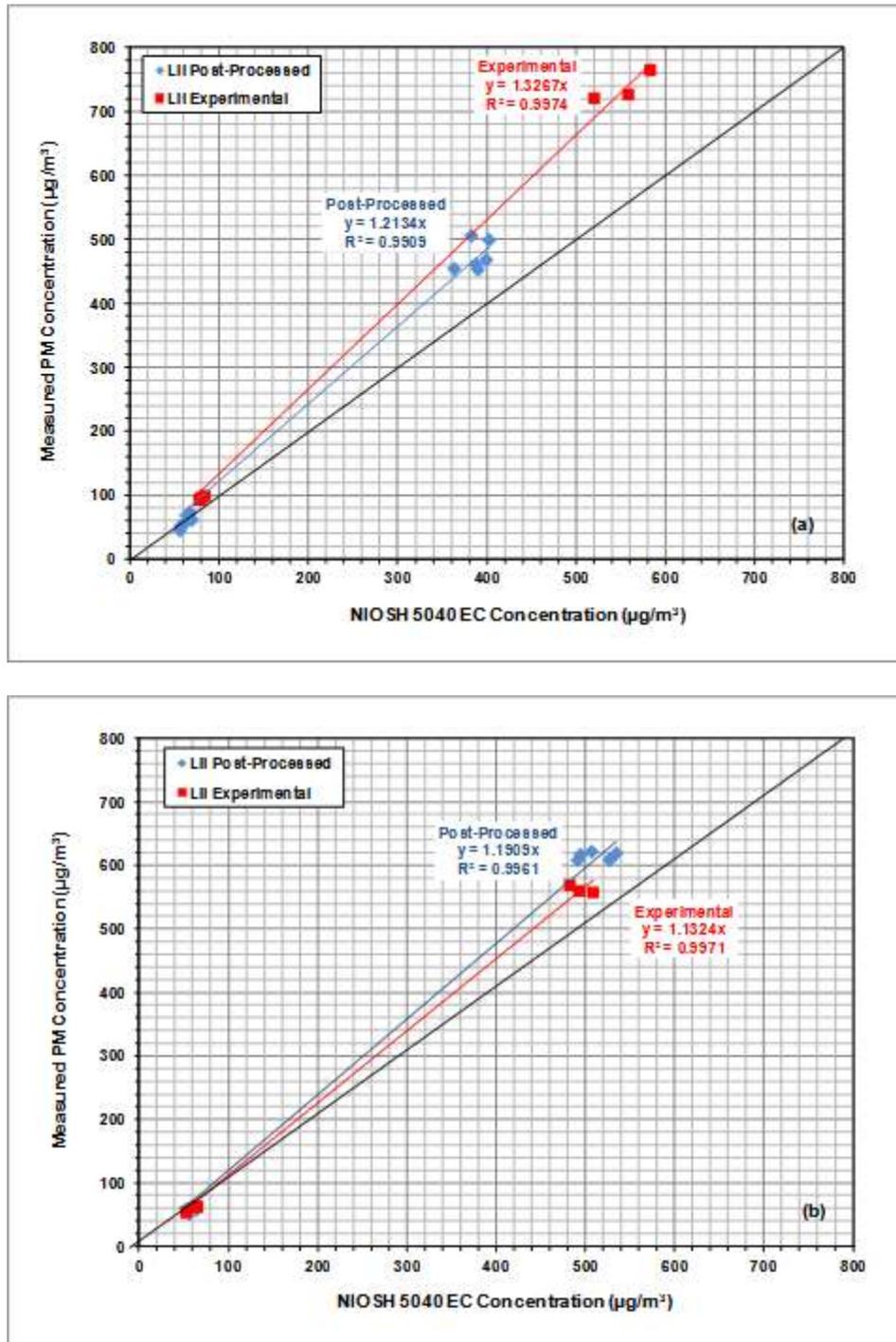


Figure J-2. Comparison of LII post-processed data to new experimental results based on NIOSH 5040 measurements for tests (a) with stripper and (b) without stripper.

## 2.0 VERIFICATION OF SUPERMAAP RESULTS

A similar evaluation was also conducted for the SuperMAAP, except only data collected with the CS (three tests at  $50 \mu\text{g}/\text{m}^3$  and three at  $500 \mu\text{g}/\text{m}^3$  concentrations) are shown in Figures J-3 and J-4. The unstriped results were highly suspect and thus deleted from this analysis. As shown in the figures, both slopes (experimental and post-processed) were almost the same when compared with OC-corrected Teflon results and within 7% when compared with NIOSH EC. These results indicate good agreement between repeated laboratory experiments and the computer-based post-processing method using the newly developed LabView post-processor. These results allowed us to use the post-processed SuperMAAP results without repeating all experiments.

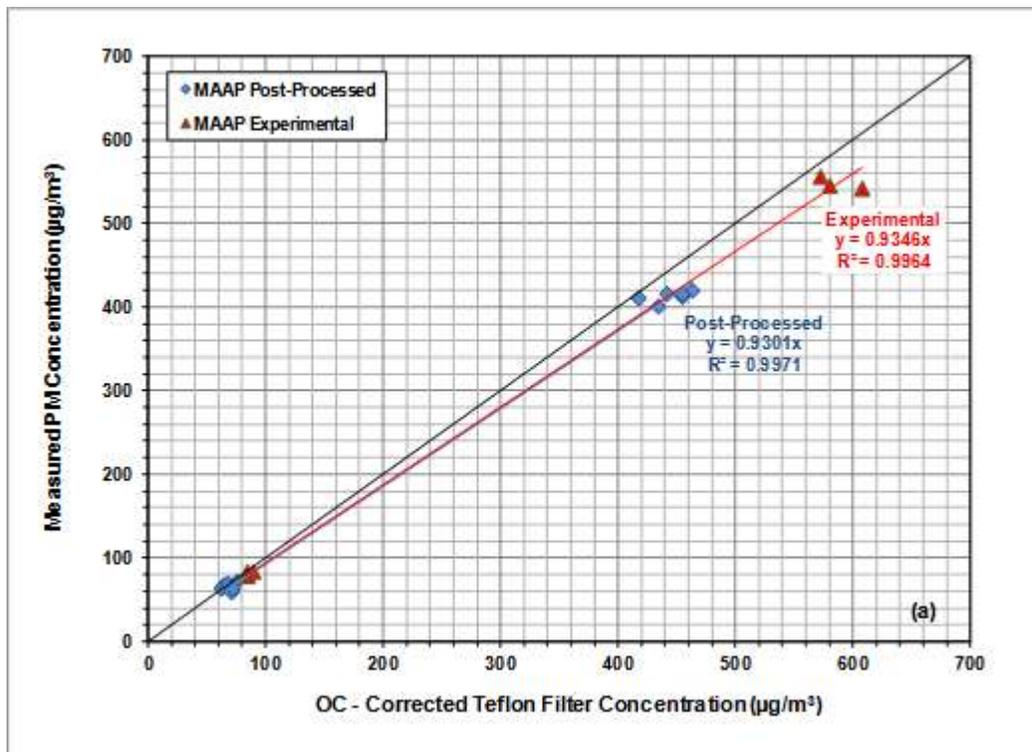


Figure J-3. Comparison of SuperMAAP post-processed data to new experimental results based on Teflon filter measurements for tests with stripper.

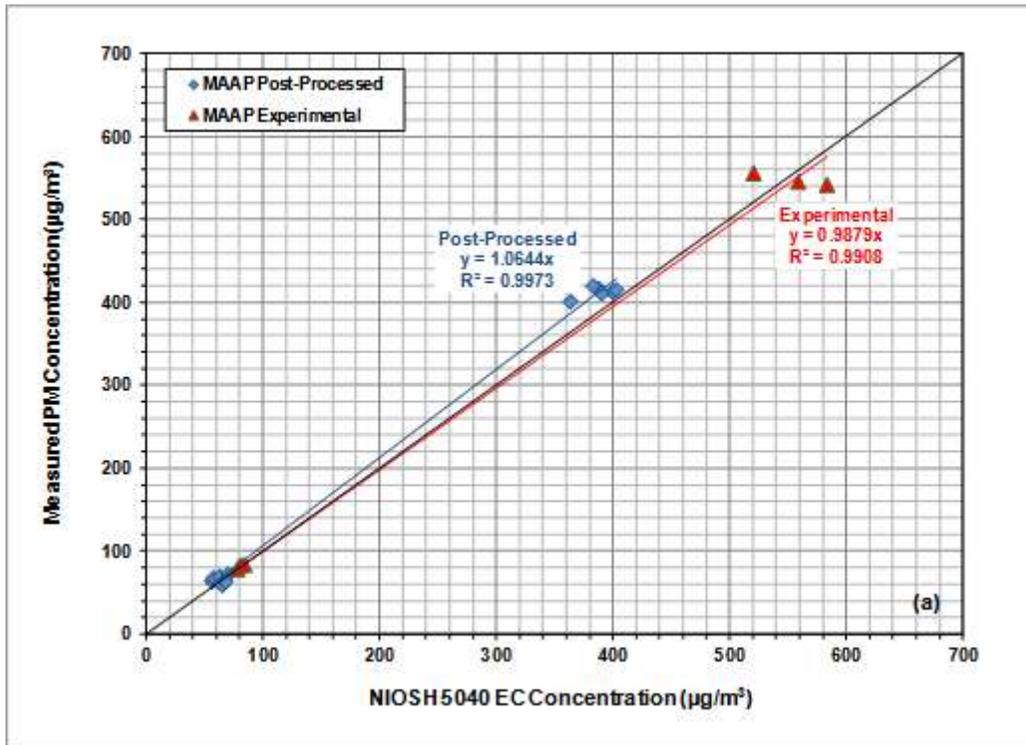


Figure J-4. Comparison of SuperMAAP post-processed data to new experimental results based on NIOSH 5040 measurements for tests with stripper.

# Appendix K: APPCD Metrology Laboratory Calibration Reports

NRMRL/APPCD



US EPA APPCD Metrology Lab

Flow Rate Evaluation Report

<b>Device Under Test</b>	Micro Soot Measuring System	<b>Calibration Date</b>	4/25/2011
<b>Mfr., Model</b>	AVL, BO6529	<b>Location</b>	High Bay
<b>Serial Number</b>	273	<b>Notebook, page</b>	2273, p. 70
<b>Met. Lab ID</b>	03743		
<b>Affiliation &amp; PI</b>	NRMRL, APPCD, ECPB, John Kinsey	<b>Ambient Conditions During Calibration</b>	
<b>Requestor</b>	Jelica Pavlovic	Temperature between 20 °C and 24 °C	
<b>Report File</b>	AVL 03743 2011-04-25 qa.xls	RH between 30 % and 60 %	
<b>MOP #</b>	FV-0237.0	Pressure between 1,000 hPa and 1,005 hPa	

Comments

Flow rate was evaluated at a single point. The unit was found to operate within the manufacturer's specified tolerances of 10% of target flow rate.

Data and Results

<u>Reference Flow Rate,</u>	<u>DUT Flow Rate, LPM</u>	<u>Difference, LPM</u>
LPM		
3.819	3.80	-0.02

Difference from Target was -0.5 %

Test Equipment

<u>Device</u>	<u>Calibration Due</u>	<u>SN</u>	<u>Uncertainty (2K)</u>
Gilibrator 2 6 LPM cell	11/8/2011	1011020-S	±1.0 % Reading

Evaluated by Mike Tufts

US EPA APPCD Metrology Lab

Flow Rate Calibration Report

<b>Device Under Test</b>	QFF Flow Rate	<b>Calibration Date</b>	7/6/2011
<b>Mfr., Model</b>	Dwyer, GFC1133	<b>Location</b>	Soot Tunnel Lab
<b>Serial Number</b>	G1013521C	<b>Notebook, page</b>	2273, p. 119
<b>Met. Lab ID</b>	02811	<b>Ambient Conditions During Calibration</b>	
<b>Affiliation &amp; PI</b>	NRMRL, APPCD, ECPB, John Kinsey	Temperature between 21 °C and 25 °C	
<b>Requestor</b>	Jelica Pavlovik	RH between 20 % and 50 %	
<b>Report File</b>	MFC 02811 2011-07-06 qa.xls	Pressure between 1,001 hPa and 1,007 hPa	
<b>MOP #</b>	FV-0237.0		

Comments

MFC flow rate response was compared to flow rate measured with a Bios DryCal. A strong vacuum (23 "Hg) was pulled on the outlet of the MFC to draw room air through the DryCal then the MFC. This calibration is only valid for 5 SLPM to 20 SLPM and in the configuration in which it was calibrated.

Correction Equation and Uncertainty

Use the equation format below to correct a device response.

$$y = m * x + b$$

Coefficients for correcting a device response, y = corrected response (SLPM) and x = device response (Volts)

$$m = 10.011, b = -0.335$$

Correction equations were derived from least squared methods and will reduce systematic bias from DUT measurements. Flow rate was corrected to standard conditions of 25.0 °C (77 °F) and 1013.25 hPa (1 atm.).

Combined Expanded Uncertainty for this calibration was ± 0.38 % of reading and ± 0.29 SLPM.

Combined Expanded Uncertainty includes random errors after correction, DUT resolution, and uncertainty of reference devices. It is expressed at a coverage factor of 2 representing a confidence interval of approximately 95%.

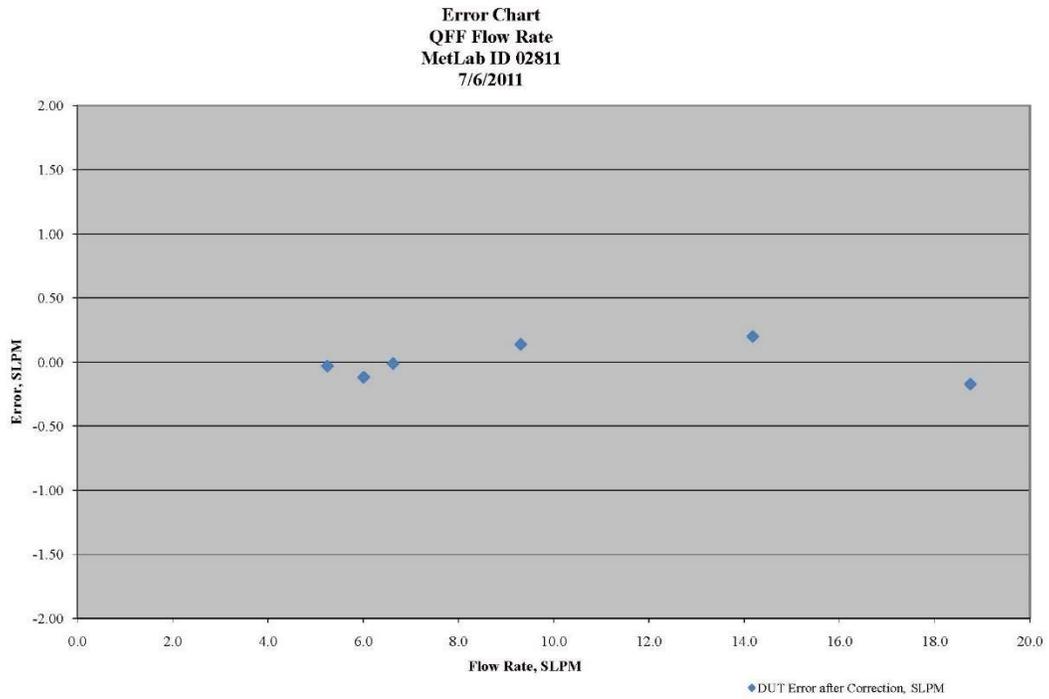
Test Equipment			
Device	Calibration Due	SN	Uncertainty (2K)
DryCal, 0.05-50 L/min	10/3/2012	H1688	±1% of reading

Calibrated by Mike Tufts

**Measurement Results**

**DUT Name** QFF Flow Rate  
**MetLab ID** 02811  
**Calibration Date** 7/6/2011

DUT Response, Volts	Reference Measurement, SLPm	Corrected DUT Reading, SLPm	DUT Error after Correction, SLPm
1.889	18.75	18.58	-0.17
1.470	14.18	14.38	0.20
0.977	9.31	9.45	0.14
0.694	6.63	6.62	-0.01
0.555	5.25	5.22	-0.03
0.622	6.01	5.89	-0.12



US EPA APPCD Metrology Lab

Flow Rate Calibration Report

<b>Device Under Test</b>	Small Soot Tunnel Blower	<b>Calibration Date</b>	4/28/2011
<b>Mfr., Model</b>	Fuji Electric, VFC200A-7W	<b>Location</b>	high bay
<b>Serial Number</b>	10577484	<b>Notebook, page</b>	2273, p. 69 & 75
<b>Met. Lab ID</b>	03735		
<b>Affiliation &amp; PI</b>	NRMRL, APPCD, ECPB, John Kinsey	<b>Ambient Conditions During Calibration</b>	
<b>Requestor</b>	Jelica Pavlovic	Temperature between 18 °C and 22 °C	
<b>Report File</b>	blower 03735 2011-04-28 qa.xls	RH between 30 % and 60 %	
<b>MOP #</b>	FV-0236.0	Pressure between 1,001 hPa and 1,007 hPa	

Comments

Calibration was performed by comparing blower frequency drive set points to flow rate measured with the M175 Roots meter. Calibration gas was room air.

Correction Equation and Uncertainty

Use the equation format below to correct a device response.

$$y = A2 * x^2 + A1 * x + A0$$

Coefficients for correcting a device response, y = corrected response (CFM) and x = device response (Hz)

$$A2 = -3.488E-04, A1 = 6.180E-01, A0 = -0.660$$

Correction equations were derived from least squared methods and will reduce systematic bias from DUT measurements.

Combined Expanded Uncertainty for this calibration was ± 0.76 % of reading and ± 0.15 CFM.

Combined Expanded Uncertainty includes random errors after correction, DUT resolution, and uncertainty of reference devices. It is expressed at a coverage factor of 2 representing a confidence interval of approximately 95%.

Device	Test Equipment		
	Calibration Due	SN	Uncertainty (2K)
Roots Meter 5M175	9/25/2015	0521990	±1.0%
ASL F250	6/10/2011	2169 018 1204	± 0.02 °C
ASL T-100 SPRT A	3/9/2012	400054	±0.02 °C
Heise HQS-2, 0-30 PSIA	7/11/2008	20400	±0.38 mmHg

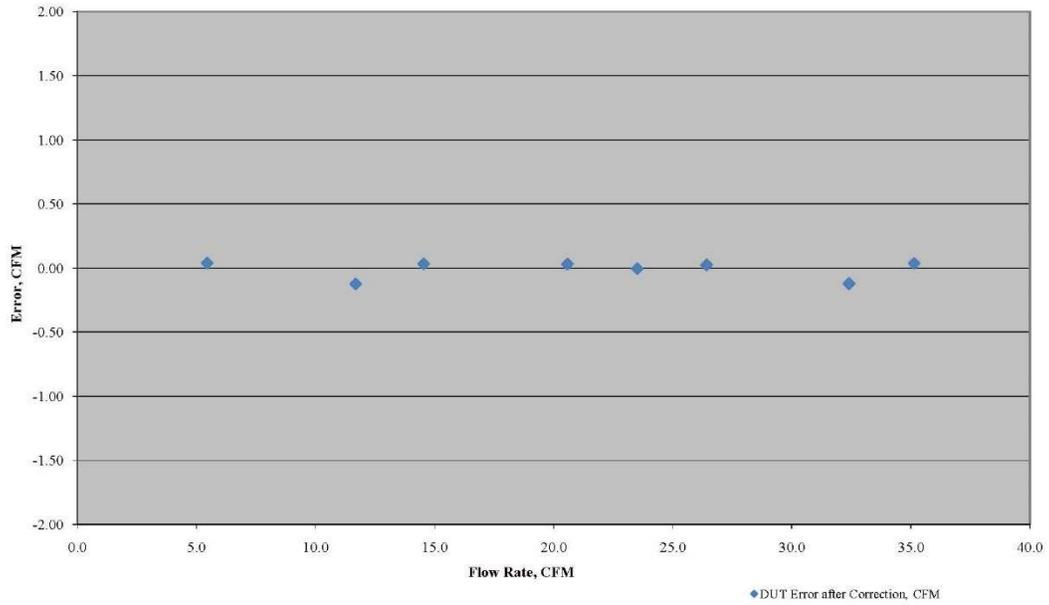
Calibrated by Mike Tufts

**Measurement Results**

**DUT Name**            Small Soot Tunnel Blower  
**MetLab ID**           03735  
**Calibration Date**   4/28/2011

DUT Set Point, Hz	Reference Measurement, CFM	Corrected DUT Reading, CFM	DUT Error after Correction, CFM
40.0	23.51	23.50	-0.01
55.0	32.40	32.27	-0.12
45.0	26.42	26.44	0.02
35.1	20.57	20.60	0.03
25.0	14.54	14.57	0.03
20.0	11.69	11.56	-0.12
10.0	5.45	5.49	0.04
60.0	35.13	35.16	0.04

**Error Chart**  
**Small Soot Tunnel Blower**  
**MetLab ID 03735**  
**4/28/2011**



US EPA APPCD Metrology Lab

Flow Rate Calibration Report

<b>Device Under Test</b>	Large Soot Tunnel Blower	<b>Calibration Date</b>	4/27/2011
<b>Mfr., Model</b>	Fuji Electric, VFC400A-7W	<b>Location</b>	high bay
<b>Serial Number</b>	0311J77486120	<b>Notebook, page</b>	2273, p. 69 & 75
<b>Met. Lab ID</b>	03744		
<b>Affiliation &amp; PI</b>	NRMRL, APPCD, ECPB, John Kinsey	<b>Ambient Conditions During Calibration</b>	
<b>Requestor</b>	Jelica Pavlovic	Temperature between 18 °C and 22 °C	
<b>Report File</b>	blower 03744 2011-04-27 qa.xls	RH between 30 % and 60 %	
<b>MOP #</b>	FV-0236.0	Pressure between 1,001 hPa and 1,007 hPa	

Comments

Calibration was performed by comparing blower frequency drive set points to flow rate measured with the M175 Roots meter. Calibration gas was room air.

Correction Equation and Uncertainty

Use the equation format below to correct a device response.

$$y = A2 * x^2 + A1 * x + A0$$

Coefficients for correcting a device response, y = corrected response (CFM) and x = device response (Hz)

$$A2 = -8.632E-04, A1 = 1.386E+00, A0 = -1.182$$

Correction equations were derived from least squared methods and will reduce systematic bias from DUT measurements.

Combined Expanded Uncertainty for this calibration was ± 0.89 % of reading and ± 0.18 CFM.

Combined Expanded Uncertainty includes random errors after correction, DUT resolution, and uncertainty of reference devices. It is expressed at a coverage factor of 2 representing a confidence interval of approximately 95%.

Device	Test Equipment		
	Calibration Due	SN	Uncertainty (2K)
Roots Meter 5M175	9/25/2015	0521990	±1.0%
ASL F250	6/10/2011	2169 018 1204	± 0.02 °C
ASL T-100 SPRT A	3/9/2012	400054	±0.02 °C
Heise HQS-2, 0-30 PSIA	7/11/2008	20400	±0.38 mmHg

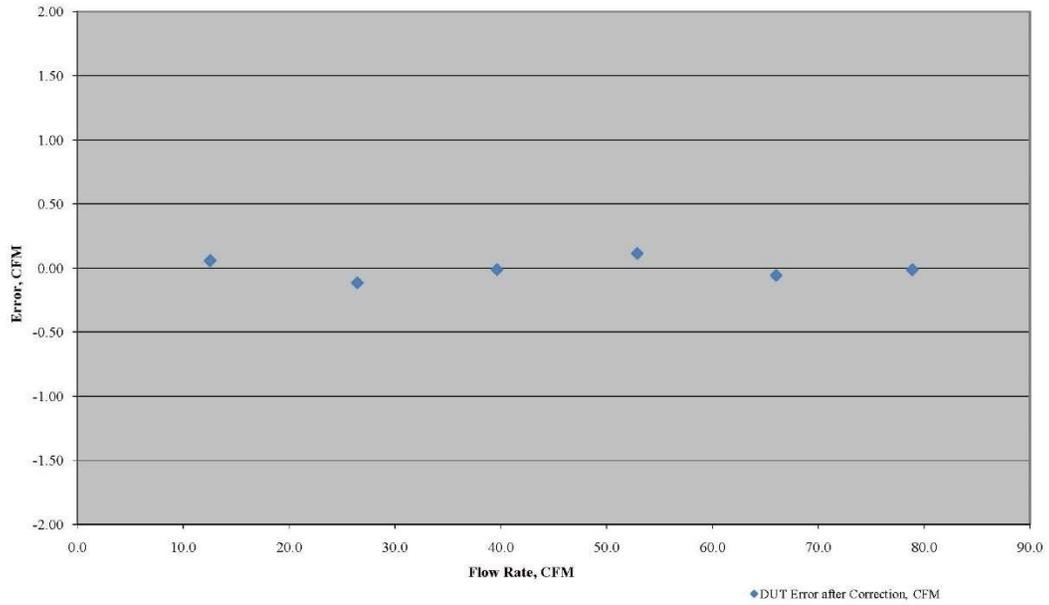
Calibrated by Mike Tufts

**Measurement Results**

**DUT Name**            Large Soot Tunnel Blower  
**MetLab ID**            03744  
**Calibration Date**    4/27/2011

DUT Set Point, Hz	Reference Measurement, CFM	Corrected DUT Reading, CFM	DUT Error after Correction, CFM
10.0	12.53	12.59	0.06
20.1	26.44	26.33	-0.12
30.0	39.63	39.62	-0.01
40.1	52.90	53.01	0.11
50.0	66.02	65.96	-0.06
60.0	78.89	78.87	-0.02

**Error Chart**  
**Large Soot Tunnel Blower**  
**MetLab ID 03744**  
**4/27/2011**



US EPA APPCD Metrology Lab

Flow Rate Calibration Report

<b>Device Under Test</b>	LII Rotameter	<b>Calibration Date</b>	5/4/2011
<b>Mfr., Model</b>	Dwyer, none	<b>Location</b>	High Bay
<b>Serial Number</b>	none	<b>Notebook, page</b>	2273, p. 78
<b>Met. Lab ID</b>	03040	<b>Ambient Conditions During Calibration</b>	
<b>Affiliation &amp; PI</b>	NRMRL, APPCD, ECPB, John Kinsey	Temperature between 19 °C and 23 °C	
<b>Requestor</b>	Jelica Pavlovic	RH between 30 % and 60 %	
<b>Report File</b>	rotameter 03040 2011-05-04 qa.xls	Pressure between 1,004 hPa and 1,009 hPa	
<b>MOP #</b>	FV-0237.0		

Comments

Calibration was performed by comparing rotameter readings to the DryCal measured flow rate. The rotameter was read at the center of the ball. Calibrated only at the anticipated flow rate of the LII.

Range: 0.5 to 10 LPM

Correction Equation and Uncertainty

Use the equation format below to correct a device response.

$$y = m * x + b$$

Coefficients for correcting a device response, y = corrected response (SLPM) and x = device response (LPM)

$$m = 0.88, b = -2.3$$

Correction equations were derived from least squared methods and will reduce systematic bias from DUT measurements. Flow rate was corrected to standard conditions of 25.0 °C (77 °F) and 1013.25 hPa (1 atm.).

Combined Expanded Uncertainty for this calibration was ± 0.15 SLPM.

Combined Expanded Uncertainty includes random errors after correction, DUT resolution, and uncertainty of reference devices. It is expressed at a coverage factor of 2 representing a confidence interval of approximately 95%.

Test Equipment			
Device	Calibration Due	SN	Uncertainty (2K)
DryCal, 0.05-50 L/min	10/3/2011	H1688	±1% of reading

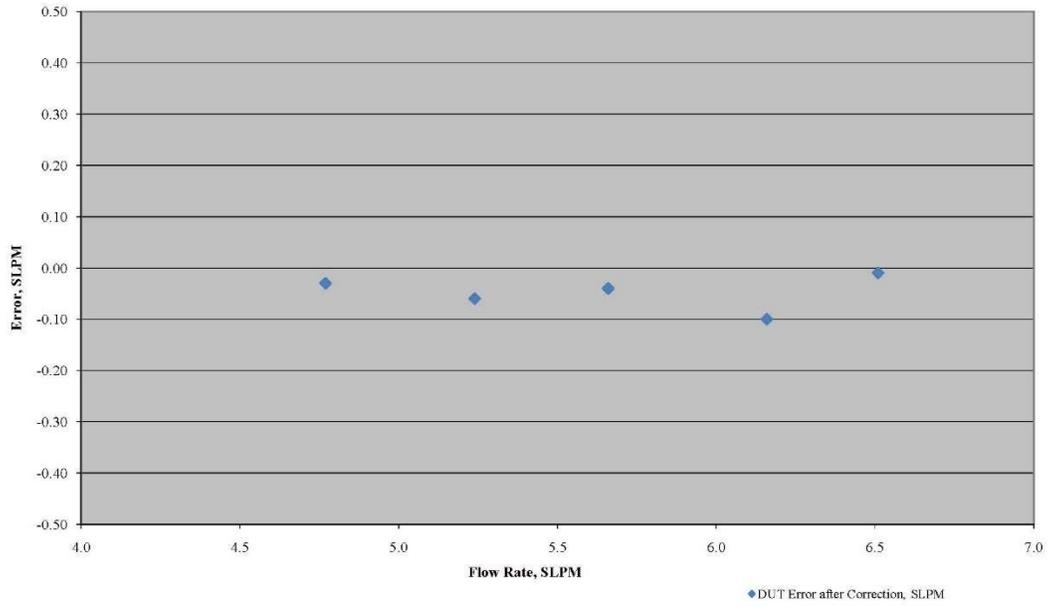
Calibrated by Mike Tufts

**Measurement Results**

**DUT Name** LII Rotameter  
**MetLab ID** 03040  
**Calibration Date** 5/4/2011

DUT Set Point, LPM	Reference Measurement, SLPM	Corrected DUT Reading, SLPM	DUT Error after Correction, SLPM
8.0	4.77	4.74	-0.03
8.5	5.24	5.18	-0.06
9.0	5.66	5.62	-0.04
9.5	6.16	6.06	-0.10
10.0	6.51	6.50	-0.01

**Error Chart  
LII Rotameter  
MetLab ID 03040  
5/4/2011**



US EPA APPCD Metrology Lab

Flow Rate Calibration Report

<b>Device Under Test</b>	Sample Dump Rotameter	<b>Calibration Date</b>	5/4/2011
<b>Mfr., Model</b>	Dwyer, RMC-104-SSV	<b>Location</b>	High Bay
<b>Serial Number</b>	none	<b>Notebook, page</b>	2273, p. 78
<b>Met. Lab ID</b>	03747		
<b>Affiliation &amp; PI</b>	NRMRL, APPCD, ECPB, John Kinsey	<b>Ambient Conditions During Calibration</b>	
<b>Requestor</b>	Jaleica Pavlovic	Temperature between 19 °C and 23 °C	
<b>Report File</b>	rotameter 03747 2011-05-04 qa.xls	RH between 30 % and 60 %	
<b>MOP #</b>	FV-0237.0	Pressure between 1,004 hPa and 1,009 hPa	

Comments

Calibration was performed by comparing rotameter readings to the DryCal measured flow rate. The rotameter was read at the center of the ball.

Range: 50 to 400 SCFH

Correction Equation and Uncertainty

Use the equation format below to correct a device response.

$$y = m * x + b$$

Coefficients for correcting a device response, y = corrected response (SLPM) and x = device response (SCFH)

$$m = 0.397, b = -19.0$$

Correction equations were derived from least squared methods and will reduce systematic bias from DUT measurements. Flow rate was corrected to standard conditions of 25.0 °C (77 °F) and 1013.25 hPa (1 atm.).

Combined Expanded Uncertainty for this calibration was ± 1.2 SLPM.

Combined Expanded Uncertainty includes random errors after correction, DUT resolution, and uncertainty of reference devices. It is expressed at a coverage factor of 2 representing a confidence interval of approximately 95%.

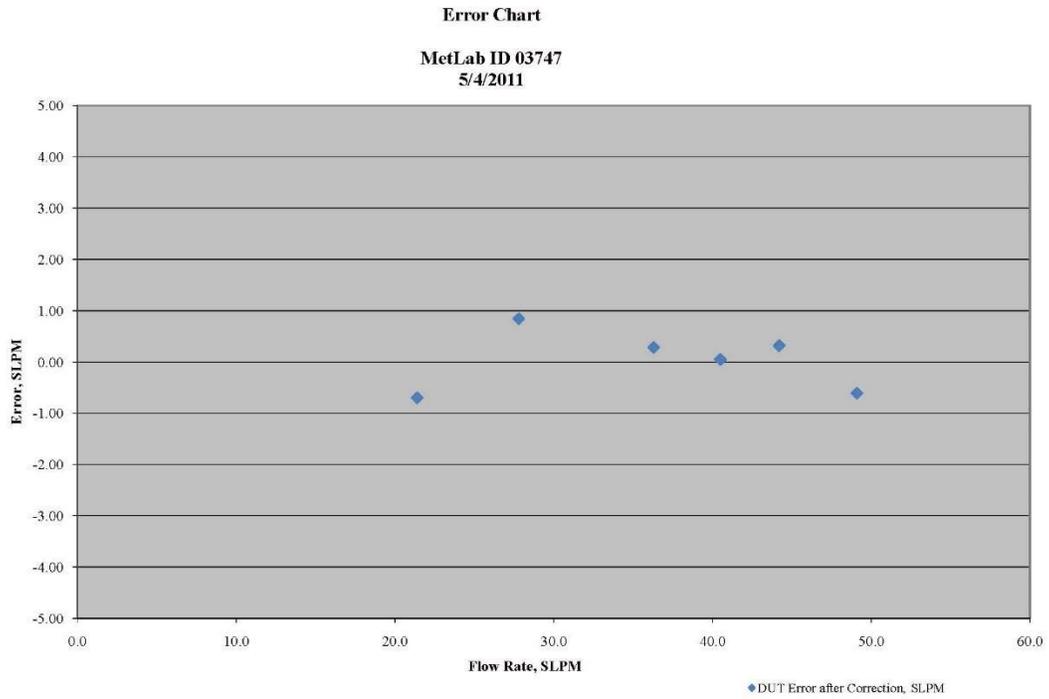
Test Equipment			
Device	Calibration Due	SN	Uncertainty (2K)
DryCal, 0.05-50 L/min	10/3/2011	H1688	±1% of reading

Calibrated by Mike Tufts

**Measurement Results**

**DUT Name**            Sample Dump Rotameter  
**MetLab ID**            03747  
**Calibration Date**    5/4/2011

DUT Set Point, SCFH	Reference Measurement, SLPM	Corrected DUT Reading, SLPM	DUT Error after Correction, SLPM
100.0	21.40	20.70	-0.70
120.0	27.80	28.64	0.84
140.0	36.30	36.58	0.28
150.0	40.50	40.55	0.05
160.0	44.20	44.52	0.32
170.0	49.10	48.49	-0.61



US EPA APPCD Metrology Lab

Pressure Calibration Report

<b>Device Under Test</b>	Orifice Plate dP Sensor	<b>Calibration Date</b>	7/21/2011
<b>Mfr., Model</b>	Omega Engineering, PX653 - 10D5V	<b>Location</b>	High Bay
<b>Serial Number</b>	20927145	<b>Notebook, page</b>	2273, p. 127
<b>Met. Lab ID</b>	03686	<b>Ambient Conditions During Calibration</b>	
<b>Affiliation &amp; PI</b>	NRMRL, APPCD, ECPB, John Kinsey	Temperature between 21 °C and 25 °C	
<b>Requestor</b>	Jelica Pavlovic	RH between 20 % and 50 %	
<b>Report File</b>	PT 03686 2011-07-21 qa.xls	Pressure between 997 hPa and 1,003 hPa	
<b>MOP #</b>	PR-0400.0		

Comments

Calibration was performed by comparing differential pressure transducer voltage response to pressure conditions generated with the Mensor APC 600.

Correction Equation and Uncertainty

Use the equation format below to correct a device response.

$$y = A3 * x^3 + A2 * x^2 + A1 * x + A0$$

Coefficients for correcting a device response, y = corrected response ("H2O) and x = device response (Volts)

$$A3 = -2.600E-03, A2 = 2.299E-02, A1 = 2.4012E+00, A0 = -2.3854$$

Correction equations were derived from least squared methods and will reduce systematic bias from DUT measurements.

Combined Expanded Uncertainty for this calibration was ± 0.003 "H2O.

Combined Expanded Uncertainty includes random errors after correction, DUT resolution, and uncertainty of reference devices. It is expressed at a coverage factor of 2 representing a confidence interval of approximately 95%.

Device	Test Equipment		
	Calibration Due	SN	Uncertainty (2K)
Mensor APC 600 10 "H2O dP cell	1/14/2012	621603-2	±0.01 % FS

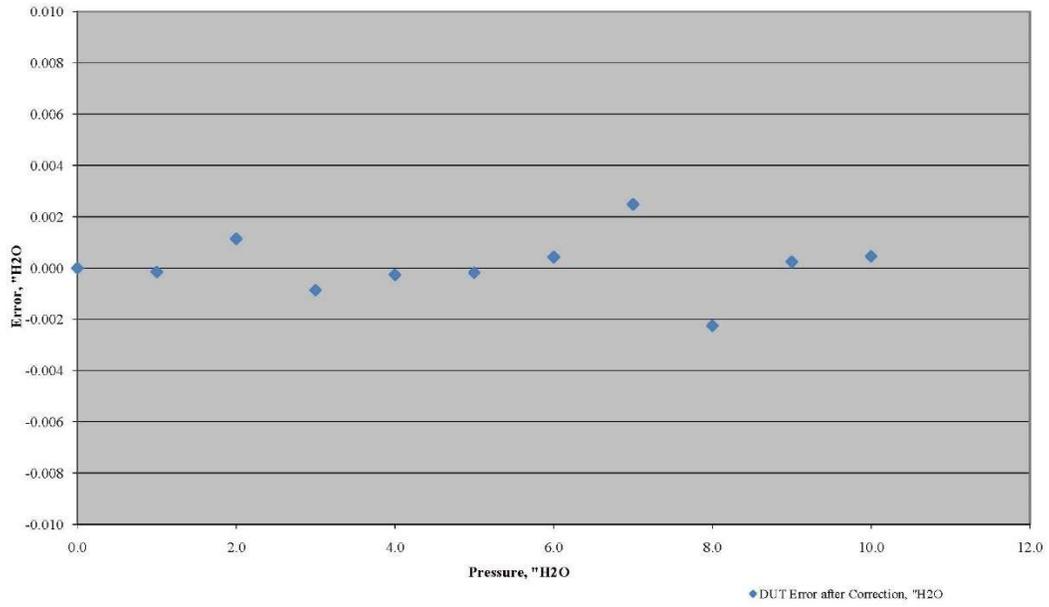
Calibrated by Mike Tufts

**Measurement Results**

**DUT Name** Orifice Plate dP Sensor  
**MetLab ID** 03686  
**Calibration Date** 7/21/2011

DUT Response, Volts	Reference Measurement, "H2O	Corrected DUT Reading, "H2O	DUT Error after Correction, "H2O
1.802	2.000	2.001	0.001
2.613	4.000	4.000	0.000
3.424	6.000	6.000	0.000
4.235	8.000	7.998	-0.002
5.053	10.000	10.000	0.000
4.644	9.000	9.000	0.000
3.830	7.000	7.002	0.002
3.018	5.000	5.000	0.000
2.207	3.000	2.999	-0.001
1.394	1.000	1.000	0.000
0.985	0.000	0.000	0.000

**Error Chart**  
**Orifice Plate dP Sensor**  
**MetLab ID 03686**  
**7/21/2011**



US EPA APPCD Metrology Lab

Flow Rate Calibration Report

<b>Device Under Test</b>	MFM431	<b>Calibration Date</b>	5/24/2011
<b>Mfr., Model</b>	Omega Engineering, FMA1728	<b>Location</b>	High Bay
<b>Serial Number</b>	G17431	<b>Notebook, page</b>	2273, p. 94
<b>Met. Lab ID</b>	02212		
<b>Affiliation &amp; PI</b>	NRMRL, APPCD, ECPB, John Kinsey	<b>Ambient Conditions During Calibration</b>	
<b>Requestor</b>	Jelica Pavlovic	Temperature between 18 °C and 22 °C	
<b>Report File</b>	MFM 02212 2011-05-24 qa.xls	RH between 30 % and 60 %	
<b>MOP #</b>	FV-0201.1	Pressure between 997 hPa and 1,003 hPa	

Comments

The correlation for this calibration was between mass flow meter response and flow rate measured with a DryCal flow calibrator. Compressed dried house air was used as the calibration gas.

This unit was interfaced to channel #2 of an IOtech cube. It was referred to as MFM431 in Pdaq

Correction Equation and Uncertainty

Use the equation format below to correct a device response.

$$y = A2 * x^2 + A1 * x + A0$$

Coefficients for correcting a device response, y = corrected response (SLPM) and x = device response (Volts)

$$A2 = 0.1372, A1 = 9.500, A0 = 0.123$$

Correction equations were derived from least squared methods and will reduce systematic bias from DUT measurements. Flow rate was corrected to standard conditions of 25.0 °C (77 °F) and 1013.25 hPa (1 atm.).

Combined Expanded Uncertainty for this calibration was ± 0.70 % of reading and ± 0.26 SLPM.

Combined Expanded Uncertainty includes random errors after correction, DUT resolution, and uncertainty of reference devices. It is expressed at a coverage factor of 2 representing a confidence interval of approximately 95%.

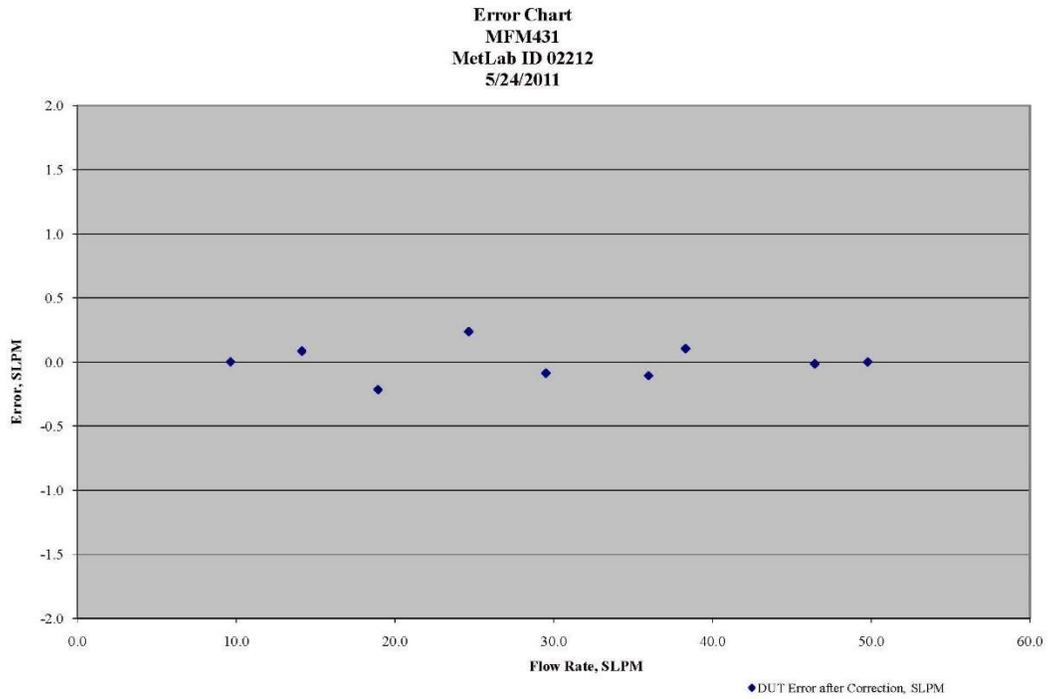
Test Equipment			
Device	Calibration Due	SN	Uncertainty (2K)
DryCal, 0.05-50 L/min	10/3/2011	H1688	±1% of reading

Calibrated by Mike Tufts

**Measurement Results**

**DUT Name** MFM431  
**MetLab ID** 02212  
**Calibration Date** 5/24/2011

DUT Response, Volts	Reference Measurement, SLPM	Corrected DUT Reading, SLPM	DUT Error after Correction, SLPM
1.904	18.93	18.71	-0.22
2.958	29.51	29.42	-0.09
3.821	38.32	38.42	0.10
4.884	49.79	49.79	0.00
4.572	46.44	46.42	-0.02
3.578	35.98	35.87	-0.11
2.515	24.65	24.89	0.24
1.453	14.13	14.21	0.08
0.988	9.64	9.64	0.00



US EPA APPCD Metrology Lab

Flow Rate Calibration Report

<b>Device Under Test</b>	MF392	<b>Calibration Date</b>	5/24/2011
<b>Mfr., Model</b>	Omega Engineering, FMA1728	<b>Location</b>	High Bay
<b>Serial Number</b>	G17392	<b>Notebook, page</b>	2273, p. 93
<b>Met. Lab ID</b>	02213		
<b>Affiliation &amp; PI</b>	NRMRL, APPCD, ECPB, John Kinsey	<b>Ambient Conditions During Calibration</b>	
<b>Requestor</b>	Jelica Pavlovic	Temperature between 18 °C and 22 °C	
<b>Report File</b>	MF392 2011-05-24 qa.xls	RH between 30 % and 60 %	
<b>MOP #</b>	FV-0201.1	Pressure between 997 hPa and 1,003 hPa	

Comments

The correlation for this calibration was between mass flow meter response and flow rate measured with a DryCal flow calibrator. Compressed dried house air was used as the calibration gas.

This unit was interfaced to channel #3 of an IOtech cube. It was referred to as MF392 in Pdaq

Correction Equation and Uncertainty

Use the equation format below to correct a device response.

$$y = A2 * x^2 + A1 * x + A0$$

Coefficients for correcting a device response, y = corrected response (SLPM) and x = device response (Volts)

$$A2 = 0.5830, A1 = 9.353, A0 = 2.590$$

Correction equations were derived from least squared methods and will reduce systematic bias from DUT measurements. Flow rate was corrected to standard conditions of 25.0 °C (77 °F) and 1013.25 hPa (1 atm.).

Combined Expanded Uncertainty for this calibration was ± 0.39 % of reading and ± 0.30 SLPM.

Combined Expanded Uncertainty includes random errors after correction, DUT resolution, and uncertainty of reference devices. It is expressed at a coverage factor of 2 representing a confidence interval of approximately 95%.

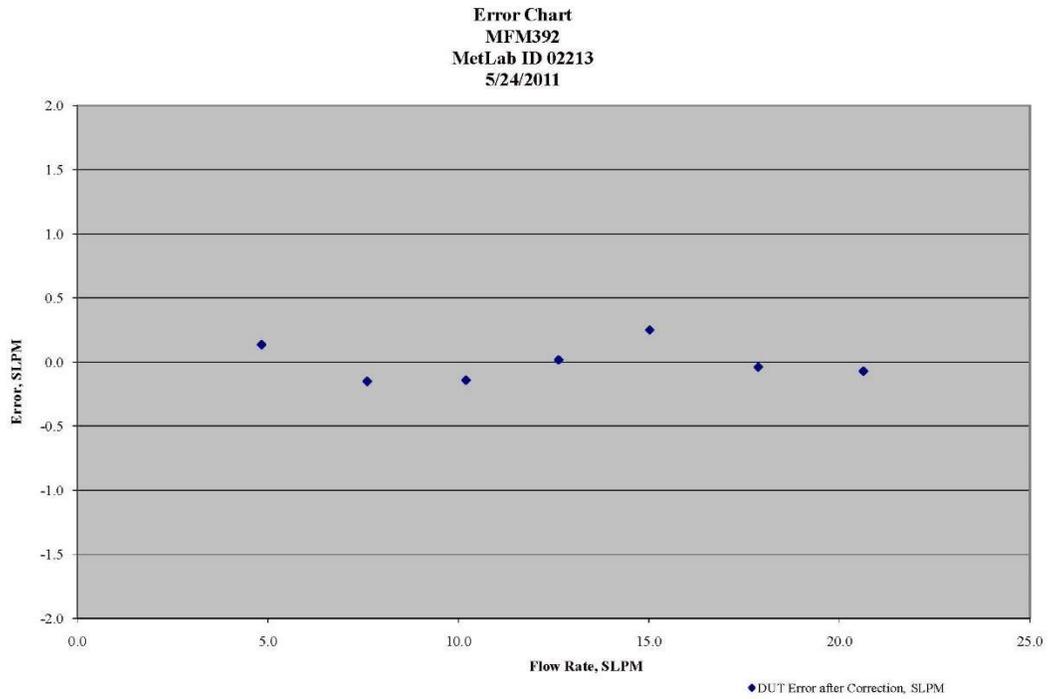
Test Equipment			
Device	Calibration Due	SN	Uncertainty (2K)
DryCal, 0.05-50 L/min	10/3/2011	H1688	±1% of reading

Calibrated by Mike Tufts

**Measurement Results**

**DUT Name** MFM392  
**MetLab ID** 02213  
**Calibration Date** 5/24/2011

DUT Response, Volts	Reference Measurement, SLPM	Corrected DUT Reading, SLPM	DUT Error after Correction, SLPM
1.734	20.63	20.56	-0.07
1.491	17.87	17.83	-0.04
1.257	15.02	15.27	0.25
1.011	12.63	12.65	0.02
0.762	10.20	10.06	-0.14
0.504	7.61	7.46	-0.15
0.250	4.83	4.97	0.14



US EPA APPCD Metrology Lab

Flow Rate Calibration Report

<b>Device Under Test</b>	Orifice Plate	<b>Calibration Date</b>	5/23/2011
<b>Mfr., Model</b>	In-house, none	<b>Location</b>	High Bay
<b>Serial Number</b>	none	<b>Notebook, page</b>	2273, p. 92
<b>Met. Lab ID</b>	03706		
<b>Affiliation &amp; PI</b>	NRMRL, APPCD, ECPB, John Kinsey	<b>Ambient Conditions During Calibration</b>	
<b>Requestor</b>	Jelica Pavlovic	Temperature between 18 °C and 22 °C	
<b>Report File</b>	OP 03706 2011-05-23 qa.xls	RH between 30 % and 60 %	
<b>MOP #</b>	FV-0201.1	Pressure between 1,001 hPa and 1,007 hPa	

Comments

The correlation for this calibration was between the square root of the orifice plate differential pressure response and flow rate measured by the Molbloc flow calibration system. Compressed dried house air was used as the calibration gas. This pressure transducer was interfaced to channel #1 of an IOtech cube. It was referred to as dP in Pdaq  
 dP cell: s/n 20927145, model # PX653-10D5V, MetLab ID 02686

An additional step is required when using the equations below with an OP. The square root of the dP reading must be calculated before the first equation is applied. The result of the second equation must be squared to determine a set point.

Correction Equation and Uncertainty

Use the equation format below to correct a device response.

$$y = m * x + b$$

Coefficients for correcting a device response, y = corrected response (SLPM) and x = device response (SQRT "H2O)

$$m = 15.636, b = 1.374$$

Correction equations were derived from least squared methods and will reduce systematic bias from DUT measurements. Flow rate was corrected to standard conditions of 25.0 °C (77 °F) and 1013.25 hPa (1 atm.).

Combined Expanded Uncertainty for this calibration was ± 1.3 % of reading and ± 0.15 SLPM.

Combined Expanded Uncertainty includes random errors after correction, DUT resolution, and uncertainty of reference devices. It is expressed at a coverage factor of 2 representing a confidence interval of approximately 95%.

Test Equipment			
Device	Calibration Due	SN	Uncertainty (2K)
DryCal, 0.05-50 L/min	10/3/2011	H1688	±1% of reading

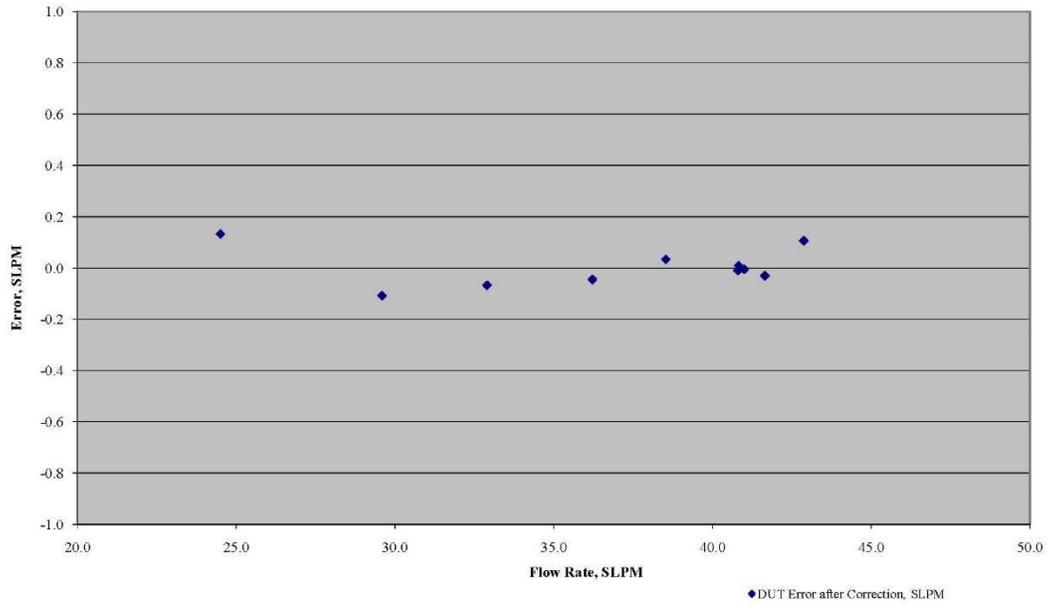
Calibrated by Mike Tufts

**Measurement Results**

**DUT Name** Orifice Plate  
**MetLab ID** 03706  
**Calibration Date** 5/23/2011

DUT Response, SQRT "H2O	Reference Measurement, SLPM	Corrected DUT Reading, SLPM	DUT Error after Correction, SLPM
1.798	29.59	29.48	-0.11
2.012	32.90	32.83	-0.07
2.226	36.22	36.17	-0.05
2.378	38.53	38.56	0.03
2.524	40.83	40.84	0.01
2.534	41.00	40.99	-0.01
2.574	41.65	41.62	-0.03
2.661	42.88	42.99	0.11
2.521	40.80	40.79	-0.01
1.488	24.50	24.63	0.13

**Error Chart**  
**Orifice Plate**  
**MetLab ID 03706**  
**5/23/2011**



US EPA APPCD Metrology Lab

Pressure Calibration Report

<b>Device Under Test</b>	PT Tunnel	<b>Calibration Date</b>	5/24/2011
<b>Mfr., Model</b>	Omega Engineering, PX309-015A5V	<b>Location</b>	High Bay
<b>Serial Number</b>	0114081007	<b>Notebook, page</b>	2273, p. 95
<b>Met. Lab ID</b>	03713	<b>Ambient Conditions During Calibration</b>	
<b>Affiliation &amp; PI</b>	NRMRL, APPCD, ECPB, John Kinsey	Temperature between 18 °C and 22 °C	
<b>Requestor</b>	Jelica Pavlovic	RH between 30 % and 60 %	
<b>Report File</b>	PT 03713 2011-05-24 qa.xls	Pressure between 997 hPa and 1,003 hPa	
<b>MOP #</b>	PR-0400.0		

Comments

The correlation for this calibration was between the pressure transducer response and the pressure condition generated by the Mensor APC600.

This unit was interfaced to channel #4 of an IOtech cube. It was referred to as PT007 in Pdaq.

Correction Equation and Uncertainty

Use the equation format below to correct a device response.

$$y = A2 * x^2 + A1 * x + A0$$

Coefficients for correcting a device response, y = corrected response (mmHg) and x = device response (V)

$$A2 = 0.0897, A1 = 154.42, A0 = 1.186$$

Correction equations were derived from least squared methods and will reduce systematic bias from DUT measurements.

Combined Expanded Uncertainty for this calibration was ± 0.14 mmHg.

Combined Expanded Uncertainty includes random errors after correction, DUT resolution, and uncertainty of reference devices. It is expressed at a coverage factor of 2 representing a confidence interval of approximately 95%.

Device	Test Equipment		
	Calibration Due	SN	Uncertainty (2K)
Mensor APC 600 15 PSIA cell	1/15/2012	621604-2	±0.01 % FS

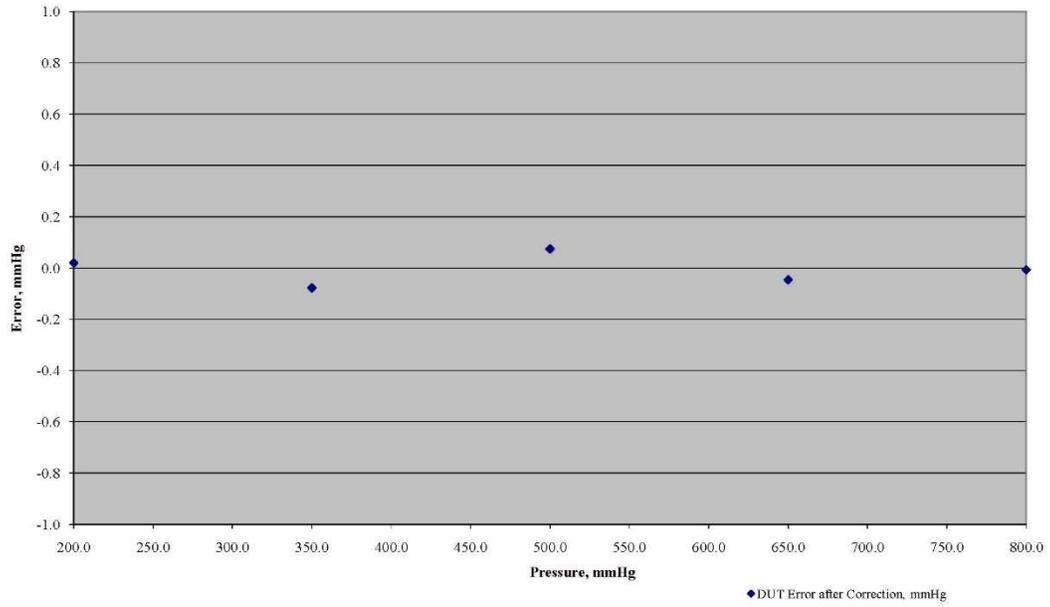
Calibrated by Mike Tufts

**Measurement Results**

**DUT Name** PT Tunnel  
**MetLab ID** 03713  
**Calibration Date** 5/24/2011

DUT Response, V	Reference Measurement, mmHg	Corrected DUT Reading, mmHg	DUT Error after Correction, mmHg
3.225	500.00	500.07	0.07
1.287	200.00	200.02	0.02
2.255	350.00	349.92	-0.08
4.191	650.00	649.95	-0.05
5.157	800.00	799.99	-0.01

**Error Chart**  
**PT Tunnel**  
**MetLab ID 03713**  
**5/24/2011**



**US EPA APPCD Metrology Lab**

**Temperature Calibration Report**

<b>Device Under Test</b>	Soot Tunnel T-Type TC	<b>Calibration Date</b>	4/20/2011
<b>Mfr., Model</b>	Omega Engineering, T-type	<b>Location</b>	high bay
<b>Serial Number</b>	none	<b>Notebook, page</b>	2183, p. 132
<b>Met. Lab ID</b>	03742	<b>Ambient Conditions During Calibration</b>	
<b>Affiliation &amp; PI</b>	NRMRL, APPCD, ECPB, John Kinsey	Temperature between 19 °C and 23 °C	
<b>Requestor</b>	Jelica Pavlovic	RH between 30 % and 60 %	
<b>Report File</b>	TC 03742 2011-04-20 qa.xls	Pressure between 1,000 hPa and 1,005 hPa	
<b>MOP #</b>	TH-0301.0		

**Comments**

Calibration was performed by comparing the response of the T-type thermocouple an data acquisition system to the conditions generated by a Hart 9170 Metrology Well.

**Correction Equation and Uncertainty**

Use the equation format below to correct a device response.

$$y = m * x + b$$

Coefficients for correcting a device response, y = corrected response (°C) and x = device response (°C)

$$m = 0.997, b = -0.055$$

Correction equations were derived from least squared methods and will reduce systematic bias from DUT measurements.

Combined Expanded Uncertainty for this calibration was ± 0.12 °C.

Combined Expanded Uncertainty includes random errors after correction, DUT resolution, and uncertainty of reference devices. It is expressed at a coverage factor of 2 representing a confidence interval of approximately 95%.

<b>Device</b>	<b>Test Equipment</b>		
	<b>Calibration Due</b>	<b>SN</b>	<b>Uncertainty (2K)</b>
Hart 9170 Metrology Well	12/2/2011	B0B515	±0.1 °C

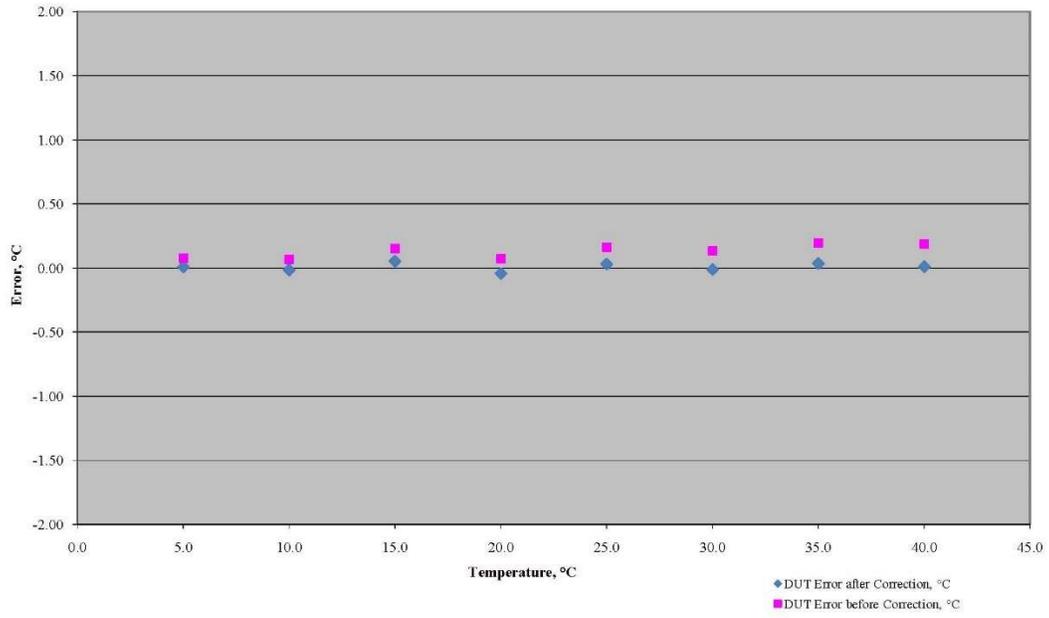
Calibrated by Mike Tufts

**Measurement Results**

**DUT Name** Soot Tunnel T-Type TC  
**MetLab ID** 03742  
**Calibration Date** 4/20/2011

DUT Response, °C	Reference Measurement, °C	Corrected DUT Reading, °C	DUT Error after Correction, °C	DUT Error before Correction, °C
30.13	30.000	29.99	-0.01	0.13
40.18	40.000	40.01	0.01	0.18
35.19	35.000	35.03	0.03	0.19
25.16	25.000	25.03	0.03	0.16
15.15	15.000	15.05	0.05	0.15
5.08	5.000	5.01	0.01	0.08
10.07	10.000	9.98	-0.02	0.07
20.07	20.000	19.96	-0.04	0.07

**Error Chart**  
**Soot Tunnel T-Type TC**  
**MetLab ID 03742**  
**4/20/2011**



US EPA APPCD Metrology Lab

Flow Rate Calibration Report

<b>Device Under Test</b>	MAAP MFC	<b>Calibration Date</b>	2/28/2012
<b>Mfr., Model</b>	MKS, M100BO1353CS1BV	<b>Location</b>	Soot Tunnel Test Facility
<b>Serial Number</b>	21698222	<b>Notebook, page</b>	2319
<b>Met. Lab ID</b>	03745	<b>Ambient Conditions During Calibration</b>	
<b>Affiliation &amp; PI</b>	NRMRL, APPCD, ECPB, John Kinsey	Temperature between 21 °C and 25 °C	
<b>Requestor</b>	Jelica Pavlovic	RH between 10 % and 40 %	
<b>Report File</b>	MFC 03745 2012-02-28 rpt maap.xls	Pressure between 1,011 hPa and 1,016 hPa	
<b>MOP #</b>	FV-0237.0		

Comments

Calibration was performed by comparing mass flow controller display set point to the flow rate measured with a dryCal flow rate calibrator. The dryCal was positioned at the inlet of the MAAP.

Flow rate data was collected at several different filter transmittance levels to determine how filter loading effected sample flow rate. Filter loading did not effect sample flow rate.

Correction Equation and Uncertainty

Use the equation format below to correct a device response.

$$y = m * x + b$$

Coefficients for correcting a device response, y = corrected response (SLPM) and x = device response (Volts)

$$m = 9.193E-01, b = -.0188$$

Correction equations were derived from least squared methods and will reduce systematic bias from DUT measurements.

Combined Expanded Uncertainty for this calibration was ± 1.0 % of reading.

Combined Expanded Uncertainty includes random errors after correction, DUT resolution, and uncertainty of reference devices. It is expressed at a coverage factor of 2 representing a confidence interval of approximately 95%.

Test Equipment

Device	Calibration Due	SN	Uncertainty (2K)
DryCal, 0.05-50 L/min	5/30/2013	H1688	±1% of reading

Calibrated by Mike Tufts

**Measurement Results**

**DUT Name** MAAP MFC  
**MetLab ID** 03745  
**Calibration Date** 2/28/2012

DUT Response, Volts	Reference Measurement, SLPM	Corrected DUT Reading, SLPM	DUT Error after Correction, SLPM
4.50	3.95	3.95	0.00
5.00	4.42	4.41	-0.01
3.50	3.04	3.03	-0.01
4.50	3.95	3.95	0.00
3.50	3.04	3.03	-0.01
3.50	3.03	3.03	0.00
4.50	3.95	3.95	0.00
4.50	3.95	3.95	-0.01
5.00	4.42	4.41	-0.01
3.50	3.03	3.03	0.00
4.50	3.94	3.95	0.00
3.50	3.03	3.03	0.00
3.50	3.03	3.03	0.00
4.50	3.95	3.95	0.00
4.50	3.94	3.95	0.01
5.00	4.41	4.41	0.00
3.50	3.03	3.03	0.00
4.50	3.94	3.95	0.01
3.50	3.03	3.03	0.00
3.50	3.03	3.03	0.00
4.50	3.94	3.95	0.01
4.50	3.94	3.95	0.01
5.00	4.41	4.41	0.00
3.50	3.03	3.03	0.00
4.50	3.94	3.95	0.01
3.50	3.03	3.03	0.00
3.50	3.03	3.03	0.00
4.50	3.94	3.95	0.01
4.50	3.94	3.95	0.01

**Error Chart**  
**MAAP MFC**  
**MetLab ID 03745**  
**2/28/2012**

